Chapter 6
Thermochemical Processes

6.1 Introduction

Biorefineries combine the necessary technologies of biorenewable feedstocks with those of chemical intermediates and final products. Recently there has been renewed interest worldwide in producing biofuels from a range of biorenewable feedstocks.

Char production by pyrolysis, bio-oil production by pyrolysis, gaseous fuels from biomass, Fischer–Tropsch liquids from biomass, hydrothermal liquefaction of biomass, supercritical liquefaction, and biochemical processes of biomass are studied and concluded in this review. Upgraded bio-oil from biomass pyrolysis can be used in vehicle engines as fuel.

The aim of a biorefinery is to extract valuable chemicals and polymers from biomass. The main technologies to produce chemicals from biomass are: (a) biomass refining or pretreatment, (b) thermochemical conversion (gasification, pyrolysis, hydrothermal upgrading), (c) fermentation and bioconversion, and (d) product separation and upgrading.

Biorefineries will use biomass as a feedstock to produce a range of chemicals similar to those currently produced from crude oil in an oil refinery. Over half of the oil produced is used to make transport fuels. In the near future, these are likely to be partly replaced with ethanol or other liquid chemicals produced from sugars and polysaccharides.

There are four main types of biorefineries: biosyngas-based refinery, pyrolysis-based refinery, hydrothermal upgrading-based refinery, and fermentation-based refinery. Biosyngas is a multi-functional intermediate for the production of materials, chemicals, transportation fuels, power and/or heat from biomass.

Thermochemical conversion (TCC) of biomass offers an efficient and economical process to provide gaseous, liquid, and solid fuels and prepare chemicals derived from biomass. TCC technologies have been studied since the eighteenth century with the first patent issued in 1788 by Robert Gardner for his work in the gasification area. However, during the span from 1800–1970 the TCC technologies were

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forgotten due to an abundance of oil. When the TCC research continued, it began to focus on sources outside of wood and coal (Midgett 2008). TCC technologies include, but are not limited to, gasification, liquefaction, pyrolysis, direct combustion, and supercritical fluid extraction. Gasification and liquefaction continue to be heavily researched and used commercially throughout the world. Researchers are focusing efforts to attempt to understand the complex reaction mechanisms that occur during these processes.

Direct combustion and co-firing with coal for electricity production from biomass is projected to be an important method in the near future. Presently, TCC technologies such as pyrolysis and gasification are not the most important options, since combustion is responsible for over 97% of the world's bioenergy production (Balat 2009). In TCC technologies such as gasification, pyrolysis, hydrothermal upgrading and supercritical water gasification, heat and sometimes pressure are the main drivers of the chemical breakdown of the fuel components. Unlike combustion, in these processes, the fuel is not fully oxidized and the process takes place in the absence of oxygen or in an oxygen-starved environment. Alternatively, the heat to drive the thermal decomposition can be provided indirectly using tubes or other heat exchange mediums.

TCC is characterized by higher temperatures and conversion rates than most other processes. TCC technologies include a continuum of processes ranging from thermal decomposition in a primarily non-reactive environment (commonly called pyrolysis) to decomposition in a chemically reactive environment (usually called gasification if the products are primarily fuel gases). Pyrolysis can be considered an incomplete gasification process, in which a mixture of gaseous, liquid and solid products is produced, each of which may have some immediate use to sustain the process. The characteristics of each of these processes can also vary depending on the oxidizing or reducing media, process temperature and process pressure.

The feedstocks for these systems vary from wood residues, agricultural residues, bark, municipal wastes, pulping liquors to mill effluents. The primary end product of these processes is either a gaseous or liquid fuel that can be cleaned and upgraded to potentially higher-value products or to produce power in a gas turbine or fuel cell. Some TCC processes, such as gasification and pyrolysis, are commercially available while others, such as supercritical gasification, are currently being investigated at the bench scale. However, none of the TCC processes has yet reached its envisioned potential as a commercially successful method to convert biomass to high-value fuels or chemicals.

Thermochemical biomass conversion does include a number of possible roots to produce from the initial biorenewable feedstock useful fuels and chemicals. Thermochemical conversion processes include three subcategories: pyrolysis, gasification, and liquefaction. Figure 6.1 shows the main biomass thermal conversion processes. Biorenewable feedstocks can be used as a solid fuel, or converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or gaseous and liquid fuels. A variety of biomass resources can be converted to liquid, solid and gaseous fuels with the help of some physical, thermochemical, biochemical and biological conversion processes. Main biomass conversion processes are direct liquefaction, indirect liquefaction, physical extraction, thermochemical conver-

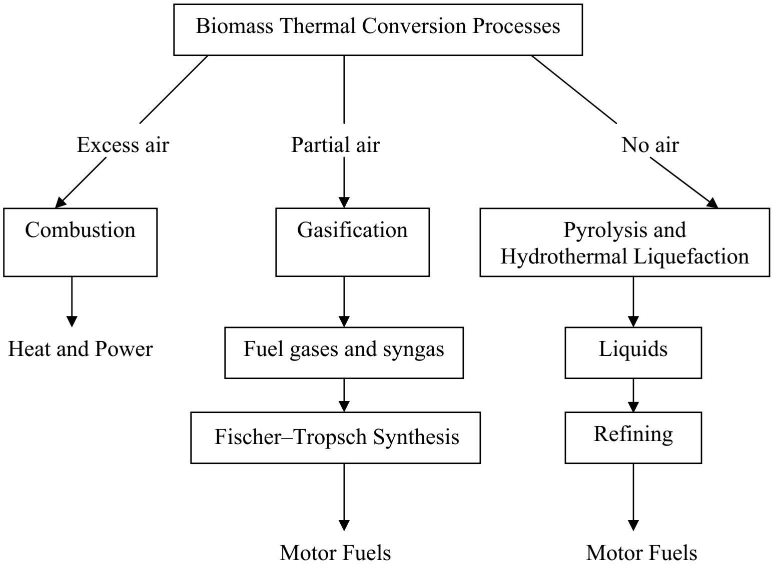


Fig. 6.1 Main biomass thermal conversion processes

sion, biochemical conversion, and electrochemical conversion (Demirbas 2001). Figure 6.2 shows in more detail the biomass thermochemical conversion processes. The conversion of biomass materials has a precise objective to transform a carbonaceous solid material which is originally difficult to handle, bulky and of low energy concentration, into the fuels having physicochemical characteristics which permit economic storage and transferability through pumping systems.

Pyrolysis is the fundamental chemical reaction process that is the precursor of both the gasification and combustion of solid fuels, and is simply defined as the

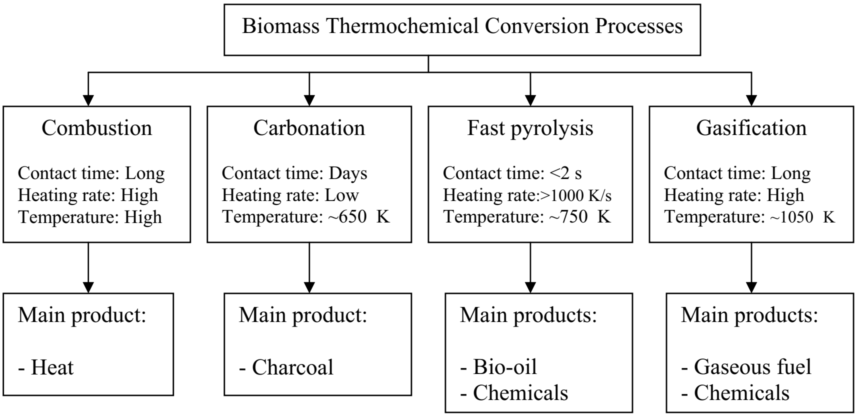


Fig. 6.2 Biomass thermochemical conversion processes with main products

chemical changes occurring when heat is applied to a material in the absence of oxygen. Gasification of biomass for use in internal combustion engines for power generation provides an important alternate renewable energy resource. Gasification is partial combustion of biomass to produce gas and char at the first stage and subsequent reduction of the product gases, chiefly CO_2 and H_2O, by the charcoal into CO and H_2. The process also generates some methane and other higher hydrocarbons depending on the design and operating conditions of the reactor.

6.2 Combustion of Biomass

Combustion is the oxidation of the fuel for the production of heat at elevated temperatures without generating commercially useful intermediate fuel gases, liquids, or solids. Combustion of MSW or other secondary materials is generally referred to as incineration. Particle temperatures in heterogeneous (e. g., unsteady reactions between solid and gas phases) combustion can differ from the surrounding gas temperatures, depending on radiation heat transfer conditions.

Combustion of solids involves the simultaneous processes of heat and mass transport, progressive pyrolysis, gasification, ignition, and burning, with no intermediate steps and with an unsteady, sometimes turbulent, fluid flow. Normally, combustion employs an excess of oxidizer to ensure maximum fuel conversion, but it can also occur under fuel-rich conditions.

Combustion is a basic chemical process that releases energy from a fuel and air mixture. For combustion to occur, fuel, oxygen, and heat must be present together. The combustion is the chemical reaction of a particular substance with oxygen. Combustion represents a chemical reaction, which is a combination of inflammable matter with oxygen of the air, accompanied by heat release. The quantity of heat produced when one mole of a hydrocarbon is burned to carbon dioxide and water is called the heat of combustion. Combustion to carbon dioxide and water is characteristic of organic compounds; under special conditions it is used to determine their carbon and hydrogen content. During combustion the combustible part of the fuel is subdivided into volatile part and solid residue. During heating it evaporates together with a part of carbon in the form of hydrocarbons combustible gases, and carbon monoxide is released by thermal degradation of the fuel. Carbon monoxide is mainly formed by the following reactions: (a) from reduction of CO_2 with unreacted C,

$$CO_2 + C \rightarrow 2CO \tag{6.1}$$

and (b) from degradation of carbonyl fragments (–CO) in the fuel molecules at 600–750 K.

The combustion process is started by heating the fuel above its ignition temperature in the presence of oxygen or air. Under the influence of heat, the chemical bonds of the fuel are cleaved. If complete combustion occurs, the combustible elements (C, H, and S) react with the oxygen content of the air to form CO_2, H_2O and mainly SO_2.

If not enough oxygen is present or the fuel and air mixture is insufficient then the burning gases are partially cooled below the ignition temperature and the combustion process stays incomplete. The flue gases then still contain combustible components, mainly carbon monoxide (CO), unburned carbon (C) and various hydrocarbons (C_xH_y).

The standard measure of the energy content of a fuel is its heating value (HV), sometimes called the calorific value or heat of combustion. In fact, there are multiple values for the HV, depending on whether it measures the enthalpy of combustion (ΔH) or the internal energy of combustion (ΔU), and whether for a fuel containing hydrogen product water is accounted for in the vapor phase or the condensed (liquid) phase. With water in the vapor phase, the lower heating value (LHV) at constant pressure measures the enthalpy change due to combustion. The heating value is obtained by the complete combustion of a unit quantity of solid fuel in an oxygen-bomb calorimeter under carefully defined conditions. The gross heat of combustion or higher heating value (GHC or HHV) is obtained by oxygen-bomb calorimeter method as the latent heat of moisture in the combustion products is recovered.

6.3 Liquefaction Process

In the liquefaction process, biomass is converted to liquefied products through a complex sequence of physical structure and chemical changes. In the liquefaction, biomass is decomposed into small molecules. These small molecules are unstable and reactive, and can repolymerize into oily compounds with a wide range of molecular weight distribution. Liquefaction is a slower form of pyrolysis that is generally performed in a pressurized batch reactor. The product bio-oil from liquefaction tends to be more viscous and has lower oxygen content than the product from fast pyrolysis.

Processes relating to liquefaction of biomass are based on the early research of Appell et al. (1971). These workers reported that a variety of biomass such as agricultural and civic wastes could be converted, partially, into a heavy oil-like product by reaction with water and carbon monoxide/hydrogen in the presence of sodium carbonate.

Liquefaction of biomass is accomplished by natural, direct and indirect thermal, extraction, and fermentation methods. Modern development of the liquefaction process can be traced to the early work at the Bureau of Mines as an extension of coal liquefaction research (Appell et al. 1971). In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Molten et al. 1983).

The pyrolysis and direct liquefaction with water processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted

Table 6.1 Comparison of liquefaction and pyrolysis

Process	Temperature (K)	Pressure (MPa)	Drying
Liquefaction	525–600	5–20	Unnecessary
Pyrolysis	650–800	0.1–0.5	Necessary

into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Molten et al. 1983). With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase. The differences in operating conditions for liquefaction and pyrolysis are shown in Table 6.1.

Liquefaction processes result in liquid product, which can be easily stored and transported and require lower process temperatures. Due to these advantages, it is becoming increasingly evident that liquid products offer more potential for the production of bio-based products than gas products and this is reflected in the rapid development of these processes and the large amount of research in this area (Mohan et al. 2006).

6.3.1 Direct Liquefaction

Direct liquefaction of wood by catalyst was carried out in the presence of K_2CO_3 (Ogi et al. 1985). Direct combustion is the oldest method for using biomass, and it still accounts for over 97% of the world's bioenergy production.

Aqueous liquefaction of lignocellulosic materials involves disaggregation of the wood ultrastructure followed by partial depolymerization of the constitutive families (hemicelluloses, cellulose, and lignin). Solubilization of the depolymerized material is then possible (Chornet and Overend 1985). The heavy oil obtained from the liquefaction process was a viscous tarry lump, which sometimes caused troubles in handling. For this purpose, some organic solvents were added to the reaction system. Among the organic solvents tested, propanol, butanol, acetone, methyl ethyl ketone and ethyl acetate were found to be effective on the formation of heavy oil having low viscosity (Demirbas 2000).

The changes during the liquefaction process involve all kinds of processes such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation. Solvolysis results in micellar-like substructures of the biomass. The depolymerization of biomass leads to smaller molecules. It also leads to new molecular rearrangements through dehydration and decarboxylation. When hydrogen is present, hydrogenolysis and hydrogenation of functional groups, such as hydroxyl groups, carboxyl groups, and keto groups also occur. Figure 6.3 shows the procedures for separation of aqueous liquefaction products.

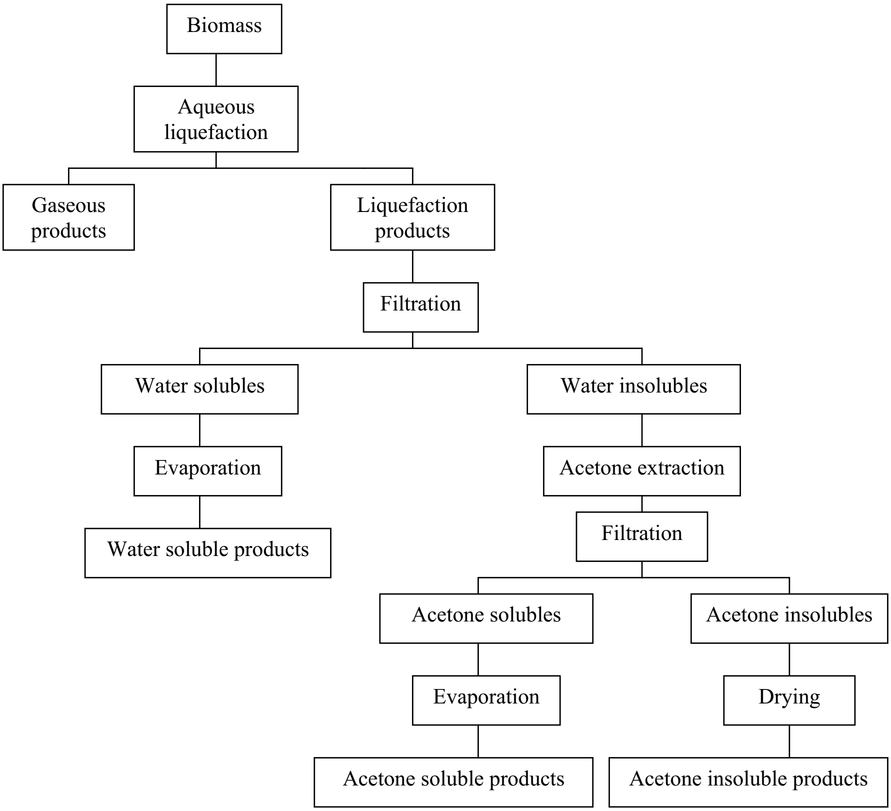


Fig. 6.3 Procedures for separation of aqueous liquefaction products

Research on direct liquefaction has been widely studied in the past, especially in the late 1970s and early 1980s for the purpose of alternative energy production. The feedstocks mainly consisted of wood and municipal solid wastes (MSW). Since then, many aspects of the process are still being studied: the type and condition of various feedstocks, the operating carrier media, and reducing reagents. More specifically researchers are focusing on various operating conditions, such as pH, processing gas, temperature, pressure, catalyst, retention time, solid content, gas-to-volatile solid ratio, and solvents for extraction or processing. In addition to studying these conditions researchers are still focusing efforts to understand the complex reactions that occur during the process. Biomass is complex by nature and varies by location. Developing a process that will handle many biomass sources, and one that is flexible to handle variations of biomass, is desired to increase the potential impact the process may have. Economics currently limit large-scale biomass liquefaction treatment facilities and on-site treatment remains difficult and expensive. However, researchers continue to move forward with their studies and many alternative organic feedstocks have been processed through this technology as a means of waste management as well as renewable energy production.

6.3.2 Indirect Liquefaction Processes

Indirect liquefaction involves successive production of an intermediate, such as synthesis gas or ethylene, and its chemical conversion to liquid fuels. In 1983, after several years of laboratory and pilot plant work on the Pittsburg Energy Research Center (PERC) process, which involves reaction of product oil or water slurries of wood particles with H_2 and CO at temperatures up to about 645 K and pressures up to 27 MPa in the presence of sodium carbonate catalyst, researchers concluded that neither process could be commercialized for liquid fuel production without substantial improvement. However, the oxygen content of the resulting complex liquid mixture is still high (6 to 10 wt.%), and considerable processing would appear to be necessary to upgrade this material (Demirbas 1992).

Alkali salts, such as sodium carbonate and potassium carbonate, can initiate the hydrolysis of cellulose and hemicellulose, into smaller fragments. The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation. In the liquefaction process, the amount of solid residue increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkyl phenols and has a complex three-dimensional structure. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin above 525 K and that the radicals have a random tendency to form a solid residue through condensation or repolymerization.

Appell and co-workers proposed the following mechanism for liquefaction of carbohydrate in the presence of sodium carbonate and carbon monoxide (Appell et al. 1967). The liquefaction mechanism is summarized in the following four steps:

1. Reaction of sodium carbonate and water with carbon monoxide, to yield sodium formate.
2. Dehydration of vicinal hydroxyl groups in a carbohydrate to an enol, followed by isomerization to ketone.
3. Reduction of newly formed carbonyl group to the corresponding alcohol with formate ion and water.
4. The hydroxyl ion reacts with additional carbon monoxide to regenerate the formate ion.

According to this mechanism, deoxygenation occurs through decarboxylation from ester formed by the hydroxyl group and formate ion derived from the carbonate.

The micellar-like broken down fragments produced by hydrolysis are then degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation. These compounds, once produced, rearrange through condensation, cyclization and polymerization, leading to new compounds (Chornet and Overend 1985). Russel et al. (1983) recognized the formation of aromatic compounds when cellulose was thermochemically converted in an alkali solution. They suggested that these aromatic compounds were formed by condensation or cyclization of unstable intermediate fragments, which were generated by degradation of the cellulose.

Basically, the alkali process involves reacting carbon monoxide with the lignocellulosic wastes in the presence of a sodium carbonate solution as a catalyst up to a temperature of 644 K and up to 28 MPa. Carbon monoxide reacts with sodium carbonate in the presence of water to form sodium formate, which, in turn, reacts with cellulose in the wood wastes to form oil and regenerate sodium carbonate. The following reactions are believed to be typical:

$$Na_2CO_3 + H_2 + 2CO \rightarrow 2HCOONa + CO_2 \tag{6.2}$$

$$2C_6H_{10}O_5 + 2HCOONa \rightarrow 2C_2H_{10}O_4 + H_2O + CO_2 + Na_2CO_3 \tag{6.3}$$

The liquefaction of biomass has been investigated in the presence of solutions of alkalis (Appell et al. 1971; Demirbas 2000), formate of alkaline metals (Appell et al. 1971; Hsu and Hixon 1981; Kucuk 2005), propanol and butanol (Demirbas 2000; Ogi and Yokokoyama 1993) and glycerol (Hsu and Hixon 1981; Demirbas 1985; Demirbas 1992; Kucuk and Demirbas 1993) or direct liquefaction (Ogi et al. 1985; Minowa et al. 1994; Demirbas 2000). In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Molten et al. 1983).

A variety of gaseous products for use as synthetic fuels and chemicals are produced by gasifying biomass. The actual product composition depends on the biomass composition and the reaction conditions. Catalytic gasification takes advantage of catalysts to serve two primary functions: (a) to increase the yield of gases, at the expense of tar and char, at lower temperatures than are possible without catalysts, and (b) to catalyze secondary reactions to produce the specific product desired. One catalytic approach to producing synthetic fuels and chemicals is indirect liquefaction of biomass, which entails gasifying the biomass to create a synthesis gas consisting of hydrogen and CO_x. These materials, in turn, are converted to the desired liquid fuels and/or chemicals by suitable choice of catalyst, synthesis gas composition, and reaction conditions.

6.3.3 Hydrothermal Conversion Processes

Hydrothermal processing offers a number of potential advantages over other biofuel production methods, including high throughputs, high energy and separation efficiency, the ability to use mixed feedstocks like wastes and lignocellulose, the production of direct replacements for existing fuels, and no need to maintain specialized microbial cultures or enzymes (Peterson et al. 2008).

Hydrothermal technologies are broadly defined as chemical and physical transformations in high-temperature (475–875 K), high-pressure (5–40 MPa) liquid or supercritical water. This thermochemical means of reforming biomass may have energetic advantages, since, when water is heated at high pressures a phase change to steam is avoided which avoids large enthalpic energy penalties. Liquefaction processes are generally lower temperature (475–675 K) reactions, which produce liquid products, often called bio-oil or biocrude. Gasification processes generally take place at higher temperatures (675–975 K) and can produce methane or hydrogen gases in high yields (Peterson et al. 2008).

The hydrothermal upgrading (HTU) process uses water as a medium in which the biomass is heated to approximately 575 K and pressurized to about 4.0 MPa in a batch reactor. The water is condensed to recover heat, and the gases are fired to provide heat for the process. The primary product is a liquid referred to as biocrude. The biocrude itself can be fired in a boiler or a kiln to provide heat, but it can also be upgraded with hydrodeoxygenation. The upgraded product can then be separated into fractions of kerosene (aviation fuel), diesel fuel (automotive fuel) and lubricating oil. Biological chemicals undergo a range of reactions, including dehydration and decarboxylation reactions, which are influenced by the temperature, pressure, concentration, and presence of homogeneous or heterogeneous catalysts. Several biomass hydrothermal conversion processes are in development or demonstration (Peterson et al. 2008).

The HTL or direct liquefaction is a promising technology to treat waste streams from various sources and produce valuable bioproducts such as biocrudes. A major problem with commercializing the HTL processes for biomass conversion today is that it remains uneconomical when compared to the costs of diesel or gasoline production. High transportation costs of large quantities of biomass increase production costs, and poor conversion efficiency coupled with a lack of understanding complex reaction mechanisms inhibits growth of the process commercially.

In the HTU process, biomass is reacted in liquid water at an elevated temperature and pressure. The phase equilibria in the HTU process are very complicated due to the presence of water, supercritical carbon dioxide, alcohols, as well as the so-called biocrude. The biocrude is a mixture with a wide molecular weight distribution and consists of various kinds of molecules. Biocrude contains 10–13% oxygen. The biocrude is upgraded by catalytic hydrodeoxygenation in a central facility. Preliminary process studies on the conversion of various biomass types into liquid fuels have indicated that HTU is more attractive than pyrolysis or gasification. In HTU the biomass, typically in a 25% slurry in water, is treated at temperatures of 575–625 K and 12–18 MPa pressures in the presence of liquid water for 5–20 min to yield a mixture of liquid biocrude, gas (mainly CO_2) and water. Subsequent processing may be able to upgrade the biocrude to useable biofuel. A large proportion of the oxygen is removed as carbon dioxide (Goudriaan and Peferoen 1990).

Biomass, such as wood, with a lower energy density is converted to biocrude with a higher energy density, organic compounds including mainly alcohols and acids, gases mainly including CO_2. Water is also a byproduct. In the products, CO_2, the main component of the gas product, can be used to represent all gas produced, and methanol and ethanol represent organic compounds. In Table 6.2, the weight fraction of each component is assigned on the basis of the data of the vacuum flash of biocrude and the data of a pilot plant (Feng et al. 2004). Figure 6.4 shows the block scheme of a commercial HTU plant. The feedstocks, reaction conditions, and the products for the HTU process are given in Table 6.3.

One of the first HTL studies was conducted by Kranich (1984) using municipal waste materials (MSW) as a source to produce oil. Three different types of materi-

Table 6.2 Representatives for the products from the HTU process

Product	Component	Weight fraction (%)
Biocrude	Polycarbonates	47.5
	Methyl-*n*-propyl ether	2.5
Gas	Carbon dioxide	25.0
Organic compounds	Methanol	5.0
	Ethanol	3.5
Water	Water	16.5

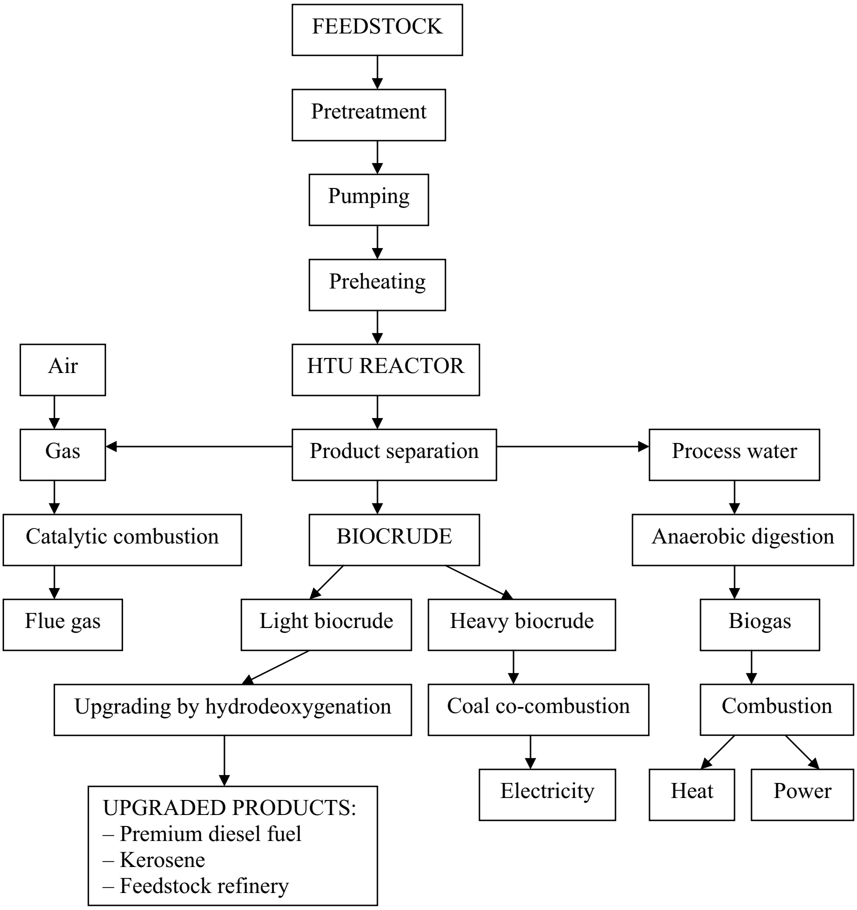


Fig. 6.4 Block scheme of commercial HTU plant

als from a MSW plant were used: primary sewage sludge, settled digester sludge, and digester effluent. Using a magnetically stirred batch autoclave with a hydrogen feed system, slurry feed device, a pressure and temperature recorder, and a wet-test meter for measuring gas product, Kranich processed the waste sources. The feed-

Table 6.3 Feedstocks, reaction conditions, and the products for the HTU process

Biomass feedstocks	Wood and forest wastes
	Agricultural and domestic residues
	Municipal solid wastes
	Organic industrial residues
	Sewage sludge
Reaction conditions	Temperature: 300–350°C
	Pressure: 12–18 MPa
	Resistance time: 5–20 min
	Medium: liquid water
Main chemical reactions	Depolymerization
	Decarboxylation
	Dehydration
	Oxygen removed as CO_2 and H_2O
	Hydrodeoxygenation
	Hydrogenation
Products (wt.% on feedstock)	Biocrude: 45
	Water-soluble organics: 10
	Gas (>90% CO_2): 25
	Process water: 20
Thermal efficiency	70–90%

stock was first dried then powdered. The wastes were also separated into different oil and water slurries and processed separately. Temperatures ranged from 570–720 K with pressures up to 14 MPa. Retention times also varied between 20–90 min. Hydrogen was used as the reducing gas with initial pressures up to 8.3 MPa. Three types of catalyst were studied: sodium carbonate, nickel carbonate, and sodium molybdate. The slurry feedstock was injected into the reactor through a pressurized injector and the oil product was extracted by pentane and toluene. Results showed that organic conversion rates varied from 45 to 99%, and oil production rates were reported from 35.0 to 63.3%. Gas products were found to contain H_2, CO_2, and C_1–C_4 hydrocarbons. The experimental results showed no significant differences between the applications of the three different catalysts. Kranich recommended that the water slurry system was not feasible for scale-up and considerations of a commercial scale process were confined to only the oil slurry system. It was also concluded that no further development work on hydroliquefaction of sewage sludge to oil was necessary. Kranich's recommendation did not hold, mainly due to increases in crude oil prices and the need to find new technologies for energy procurement, and thus many studies on liquefaction of sewage sludge have since been conducted. Research has indicated that liquefaction is a feasible method for the treatment of sewage sludge wastes and has a high oil-producing potential (Suzuki et al. 1986; Itoh et al. 1994; Inoue et al. 1997). Today HTL research is still being conducted with sewage sludge; however, focus has shifted to include many varieties of biomass materials.

Several technologies have been developed to convert biomass into a liquid biofuel with a higher heating value, such as gasification, fast pyrolysis and the HTU. In the HTU, the biomass is treated during 5–20 min with water under subcritical conditions (575–625 K, 10–18 MPa) to give a heavy organic liquid (biocrude) with a heating value of 30–35 MJ/kg. During this process, the oxygen content of the organic material is reduced from about 40% to between 10 and 15%. The removed oxygen ends up in CO_2, H_2O and CO. After 1.6 s at 595 K and 25 MPa, 47% conversion of cellulose in water was obtained yielding hydrolysis products (cellobiose, glucose, and others, 44%) and decomposition products of glucose (erythrose, 1,6-anhydroglucose, 5-hydroxymethylfurfural, 3%). Furthermore, it has been shown that cellobiose decomposes via hydrolysis to glucose and via pyrolysis to glycosylerythrose and glycosylglycolaldehyde, which are further hydrolyzed into glucose, erythrose and glycolaldehyde. Hydrolysis refers to splitting up of the organic particles into smaller organic fragments in water. Hydrothermal decomposition also acts on the large organic molecules reducing them to smaller fragments, some of which dissolve in water.

In the HTU process, biomass chips are pressurized and digested at 475–525 K with recycle water from the process. Subsequently the digested mass is pressurized to 12–18 MPa and reacted in liquid water at 575–675 K for 5–15 min. Under these conditions decarboxylation and depolymerization take place and a biocrude is formed, which separates from the water phase. Part of the process water is recycled. Obviously, the process is very simple with high efficiency.

Hydrothermal reaction involves applying heat under pressure to achieve reaction in an aqueous medium. The treatment of organic wastes by the supercritical water reaction undergoes a homogeneous phase, and interphase mass transfer limitations are avoided and reaction efficiencies of 99.9% can be achieved at residence times lower than 1 min. Because of the distinctive characteristics of water, hydrothermal reaction is an effective method for the treatment of organic wastes. The reaction can be performed under subcritical or supercritical conditions. It can also be classified into two broad categories: (1) oxidative, i. e., involving the use of oxidants, and (2) non-oxidative, i. e., excluding the use of oxidants.

6.3.4 Supercritical Liquefaction

Supercritical fluid extraction (SFE) has potential as an efficacious means of recovering secondary compounds from the lignocellulosic biomass, such as waxy lipids, terpenes and phenolics. Supercritical fluids are less viscous and diffuse more quickly than liquids and can therefore extract plant products more effectively and faster than conventional organic solvents (Gadhe et al. 2007).

Recently, supercritical fluid treatment has been considered to be an attractive alternative in the chemical reaction field. Supercritical water can be realized from the ionic reaction field to the radical reaction field. Therefore, supercritical water can act as a solvent for converting biomass into valuable substances.

Supercritical water (SCW) reforming offers several advantages over the conventional technologies because of the unusual properties of supercritical water. The density of supercritical water is higher than that of steam, which results in a high space-time yield. The higher thermal conductivity and specific heat of supercritical water is beneficial for carrying out the endothermic reforming reactions. In the supercritical region the dielectric constant of water is much lower. Furthermore, the number of hydrogen bonds is much smaller and their strength is considerably weaker. As a result, SCW behaves as an organic solvent and exhibits extraordinary solubility toward organic compounds containing large non-polar groups and most permanent gases. Another advantage of SCW reforming is that the H_2 is produced at a high pressure, which can be stored directly, thus avoiding the large energy expenditures associated with its compression. The supercritical water gasification (SCWG) process becomes economical as the compression work is reduced owing to the low compressibility of liquid feed when compared to that of gaseous H_2. Figure 6.5 shows the schematic setup of the system for supercritical water liquefaction of biomass.

In supercritical water gasification, the reaction generally takes place at the temperature over 875 K and a pressure higher than the critical point of water. With a temperature higher than 875 K, water becomes a strong oxidant, and oxygen in

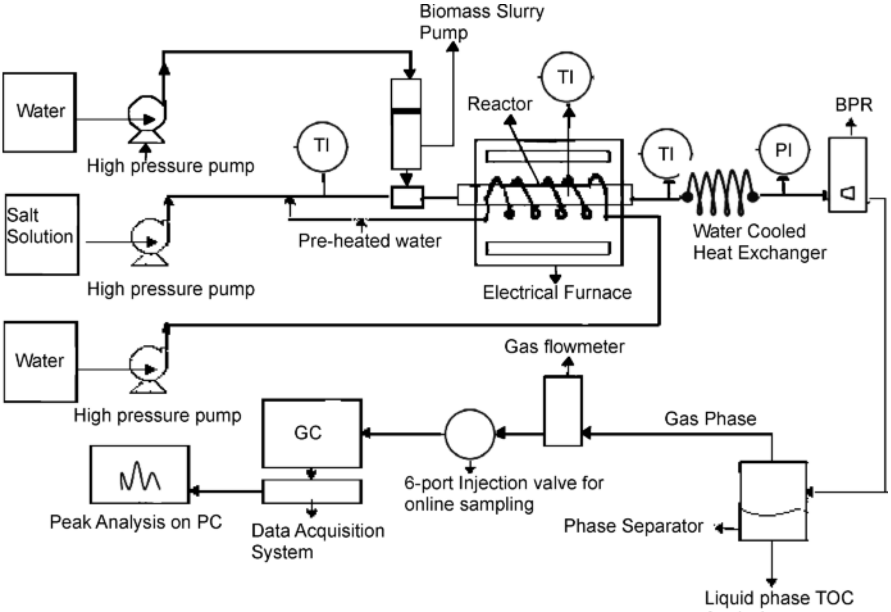


Fig. 6.5 Schematic setup of the system for supercritical water liquefaction of biomass

water can be transferred to the carbon atoms of the biomass. As a result of the high density, carbon is preferentially oxidized into CO_2 but also low concentrations of CO are formed. The hydrogen atoms of water and of the biomass are set free and form H_2. The gas product consists of hydrogen, CO_2, CH_4 and CO.

A general problem with SCWG is the required heat exchange between the reactor outlet and inlet streams. To achieve an acceptable thermal efficiency, it is crucial for the process that the heat of the inlet stream is utilized as far as possible to preheat the feedstock stream (mainly water) to reaction conditions. At the same time, heating of the biomass slurry in the inlet tube of a reactor is likely to cause fouling/plugging problems because the thermal decomposition (>525 K) starts already far below the desired reaction temperature (>875 K) (Byrd et al. 2007). In addition to being a high mass transfer effect, supercritical water also participates in reforming reaction. The molecules in the supercritical fluid have high kinetic energy like the gas and high density like the liquid. Therefore, it is expected that the chemical reactivity can be high. In addition, the ionic product and dielectric constant of supercritical water, which are important parameters for chemical reactions, can be continuously controlled by regulating pressure and temperature. Pressure has a negligible effect on hydrogen yield above the critical pressure of water. As the temperature is increased from 875 to 1075 K the H_2 yield increases from 53 to 73% by volume, respectively. Only a small amount of hydrogen is formed at low temperatures, indicating that direct reformation reaction of ethanol as a model compound in SCW is favored at high temperatures (>975 K). With an increase in the temperature, the hydrogen and carbon dioxide yields increase, while the methane yield decreases. The water excess leads to a preference for the formation of hydrogen and carbon dioxide instead of carbon monoxide. The formed intermediate carbon monoxide reacts with water to hydrogen and carbon dioxide. The low carbon monoxide yield indicates that the water–gas shift reaction approaches completion (Byrd et al. 2007).

The capillaries (1 mm ID and 150-mm-long tubular reactors) are heated rapidly (within 5 s) in a fluidized sand bed to the desired reaction temperature. Experimentation with the batch capillary method has revealed that, especially at low temperatures and high feed concentrations, char formation occurs. A fluidized bed reactor might be a good alternative to solve the problems related to this char and ash formation.

Cellulose and sawdust were gasified in supercritical water to produce hydrogen-rich gas, and Ru/C, Pd/C, CeO_2 particles, nano-CeO_2 and nano-$(CeZr)xO_2$ were selected as catalysts. The experimental results showed that the catalytic activities were Ru/C > Pd/C > nano-$(CeZr)xO_2$ > nano-CeO_2 > CeO_2 particle in turn. The 10 wt.% cellulose or sawdust with CMC can be gasified near completely with Ru/C catalyst to produce 2–4 g hydrogen yield and 11–15 g potential hydrogen yield per 100 g feedstock at the condition of 773 K, 27 MPa, 20 min residence time in supercritical water (Hao et al. 2005).

Catalysts for low-temperature gasification include combinations of stable metals, such as ruthenium or nickel bimetallics and stable supports, such as certain titania, zirconia, or carbon. Without catalyst the gasification is limited (Kruse et al. 2000). Sodium carbonate is effective in increasing the gasification efficiency of cellulose

(Minowa 1997). Likewise, homogeneous alkali catalysts have been employed for high-temperature supercritical water gasification.

Hydrogen is a sustainable, non-polluting source of energy that can be used in mobile and stationary applications. In order to evaluate hydrogen production by SCWG of various types of biomass, extensive experimental investigations have been conducted in recent years. The supercritical water reforming of biomass materials has been found to be an effective technique for the production of hydrogen with short residence times. Hydrogen production by biomass SCW is a promising technology for utilizing high moisture content biomass.

In SWC reforming, the product gases mainly consist of hydrogen and carbon dioxide, with a small amount of methane and carbon monoxide. Hydrogen yields approaching the stoichiometric limit were obtained under catalytic supercritical water conditions. Hydrogen production is influenced by temperature, residence time, and biomass concentration. The high yield of hydrogen was obtained at high reactor temperature, low residence time, and low biomass concentration. The gas product from biomass gasification in catalytic supercritical water contains about 69% H_2 and 30% CO_2 in mole fraction. Others like CH_4 and CO exist in the gas product in smaller amounts. Since a drying process is an energy-intensive operation and the produced H_2 will be stored under high-pressure supercritical water gasification is a promising technology for gasifying biomass with high moisture content.

Figure 6.6 shows the plot for the yield of bio-oils from liquefaction of corn stover at subcritical and supercritical temperatures. The yields of bio-oils increase with increasing temperature. The yield of bio-oils sharply increases between 650 and 680 K and then it reaches a plateau. This temperature range (650–680 K) is in the supercritical zone. At temperatures higher than 690 K the yield of bio-oils are slightly lower. The highest bio-oil yield of 55.7% is obtained at a reaction temperature of 680 K and the yield is 53.3% at 720 K (Demirbas 2008a).

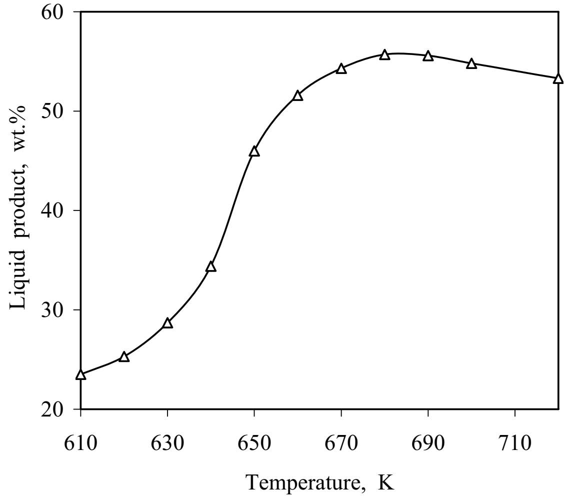


Fig. 6.6 Plot for the yield of liquid products from liquefaction of corn stover at subcritical and supercritical temperatures (liquefaction time of 70 min, water-to-solid ratio of 5:1)

6.4 Pyrolysis Process

Pyrolysis has been used since the dawn of civilization, dating back also to ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by this process. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced also condensed rapidly (Mohan et al. 2006). If some means is applied to collect the off-gases (smoke), the process is called wood distillation. The ancient Egyptians practiced wood distillation by collecting tars and pyroligneous acid for use in their embalming industry. Pyrolysis of wood to produce charcoal was a major industry in the 1800s, supplying the fuel for the industrial revolution, until it was replaced by coal. In the late nineteenth century and early twentieth century wood distillation was still profitable for producing soluble tar, pitch, creosote oil, chemicals, and non-condensable gases often used to heat boilers at the facility. The wood distillation industry declined in the 1930s due to the advent of the petrochemical industry and its lower-priced products.

Pyrolysis is the thermal decomposition of organic matter occurring in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. This is the basic thermochemical process for converting biomass to a more useful fuel. In the absence of oxygen, biomass is heated or partially combusted in a limited oxygen supply, to produce a hydrocarbon-rich gas mixture, and a carbon-rich solid residue. The products of pyrolysis can be gaseous, liquid, and/or solid. Flash pyrolysis describes the rapid, moderate temperature (675–875 K) pyrolysis that produces liquids. Biomass is heated at rates of 100 to 10 000 K/s and the vapor residence time is normally less than 2 s. The oil products are maximized at the expense of char and gas.

Pyrolysis is a process similar to gasification except generally optimized for the production of fuel liquids (pyrolysis oils) that can be used straight or refined for higher-quality uses such as engine fuels, chemicals, adhesives, and other products. Pyrolysis typically occurs at temperatures in the range of 675 to 975 K. Pyrolysis and combustion of pyrolysis-derived fuel liquids and gases also produce the same categories of end products as direct combustion of solids. Like gasification, their pollution control and conversion efficiencies may be improved.

Pyrolysis and direct liquefaction processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Demirbas 2000). With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase.

Fast pyrolysis utilizes biomass to produce a product that is used both as an energy source and a feedstock for chemical production. Considerable efforts have been made to convert wood biomass to liquid fuels and chemicals since the oil crisis in mid-1970s. Most work has been performed on wood, because of its consistency and comparability between tests. However, nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, and nut shells to energy crops such as miscanthus and sorghum. The pyrolysis reaction rate and the yield of the volatiles are determined by the biomass composition and structure, heating rate, residence time, catalyst, and particle size. Although very fast and very slow pyrolyses of biomass produce markedly different products, the variety of heating rates, temperatures, residence times, and feedstock varieties found in the literature make generalizations difficult to define, in regard to trying to critically analyze the literature (Mohan et al. 2006).

Catalytic cracking is a thermochemical process that employs catalysts using hydrogen-driven reducing reactions to accelerate the breakdown of high molecular weight compounds (e. g., plastics) into smaller products for the purpose of improving selectivity and imparting certain desirable characteristics to the final product, such as volatility and flashpoint of liquid fuels. This cracking process is often employed in oil refinery operations to produce lower molecular weight hydrocarbon fuels from waste feedstocks. These include gasoline from heavier oils, distillation residuals, and waste plastic.

Rapid heating and rapid quenching produce the intermediate pyrolysis liquid products, which condense before further reactions break down higher molecular weight species into gaseous products. High reaction rates minimize char formation. At higher fast pyrolysis temperatures, the major product is gas. If the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. For a high char production, a low temperature, low heating rate process would be chosen. If the purpose were to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred. Table 6.4 shows char, liquid and gaseous products from plant biomass by pyrolysis and gasification. It is believed that as the pyrolysis reaction progresses the carbon residue (semi-char) becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases. Pyrolysis liquids are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose, and lignin with a rapid increase in temperature. Rapid quenching traps many products that would further react (depolymerize, decompose, degrade, cleave, crack or condensate with other molecules) if the residence time at high temperature was extended (Mohan et al. 2006).

Pyrolysis is the simplest and almost certainly the oldest method of processing one fuel in order to produce a better one. Pyrolysis can also be carried out in the presence of a small quantity of oxygen (gasification), water (steam gasification) or hydrogen (hydrogenation). One of the most useful products is methane, which is a suitable fuel for electricity generation using high-efficiency gas turbines.

Cellulose and hemicelluloses form mainly volatile products on heating due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular weight fragments. The progressive increase in the pyrolysis temperature of the wood led to the release of the volatiles thus form-

Table 6.4 Char, liquid, and gaseous products from plant biomass by pyrolysis and gasification

Thermal degradation	Residence time (s)	Upper temperature (K)	Char	Liquid	Gas
Conventional pyrolysis	1800	470	85–91	7–12	2–5
	1200	500	58–65	17–24	8–14
	900	550	44–49	26–30	16–22
	600	600	36–42	27–31	23–29
	600	650	32–38	28–33	27–34
	600	850	27–33	20–26	36–41
	450	950	25–31	12–17	48–54
Slow pyrolysis	200	600	32–38	28–32	25–29
	180	650	30–35	29–34	27–32
	120	700	29–33	30–35	32–36
	90	750	26–32	27–34	33–37
	60	850	24–30	26–32	35–43
	30	950	22–28	23–29	40–48
Fast pyrolysis	5	650	29–34	46–53	11–15
	5	700	22–27	53–59	12–16
	4	750	17–23	58–64	13–18
	3	800	14–19	65–72	14–20
	2	850	11–17	68–76	15–21
	1	950	9–13	64–71	17–24
Gasification	1800	1250	7–11	4–7	82–89

ing a solid residue that is different chemically from the original starting material (Demirbas 2000). Cellulose and hemicelluloses initially break into compounds of lower molecular weight. This forms an "activated cellulose" which decomposes by two competitive reactions: one forming volatiles (anhydrosugars) and the other char and gases. The thermal degradation of the activated cellulose and hemicelluloses to form volatiles and char can be divided into categories depending on the reaction temperature. Within a fire all these reactions take place concurrently and consecutively. Gaseous emissions are predominantly a product of pyrolitic cracking of the fuel. If flames are present, fire temperatures are high, and more oxygen is available from thermally induced convection.

The biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. Products like crude bio-oil or slurry of charcoal of water or oil, have advantages in many aspects of the energy industry such as transport, storage, combustion, retrofitting and flexibility in production and marketing. Among the liquid products, methanol is one of the most valuable products. The point where the cost of producing energy from fossil fuels exceeds the cost of biomass fuels has been reached. With a few exceptions, energy from fossil fuels will cost more money than the same amount of energy supplied through biomass conversion.

Pyrolysis of wood has been studied as a zonal process with zone A (easily degrading zone) occurring at temperatures up to 475 K. The surface of the wood becomes dehydrated at this temperature, and along with water vapor, carbon dioxide, formic acid, acetic acid, and glyoxal are given off. When temperatures of 475 to 535 K are attained, the wood is said to be in zone B and is evolving water vapor, carbon dioxide, formic acid, acetic acid, glyoxal, and some carbon monoxide. The reactions to this point are mostly endothermic, the products are largely non-condensable, and the wood is becoming charred. Pyrolysis actually begins between 535 and 775 K, which is called zone C. The reactions are exothermic, and unless heat is dissipated, the temperature will rise rapidly. Combustible gases such as carbon monoxide from cleaving of carbonyl groups, methane, formaldehyde, formic acid, acetic acid, methanol, and hydrogen are being liberated and charcoal is being formed. The primary products are beginning to react with each other before they can escape the reaction zone. If the temperature continues to rise above 775 K, a layer of charcoal will be formed that is the site of vigorous secondary reactions and is classified as zone D. Carbonization is said to be complete at temperatures of 675 to 875 K. Thermal degradation properties of hemicelluloses, celluloses and lignin can be summarized as follows (Demirbas 2000):

Thermal degradation of hemicelluloses > cellulose >> lignin

If the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. For a high char production, a low temperature, low heating rate process would be chosen. If the purpose is to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred.

6.4.1 Pyrolysis Facilities

Table 6.5 shows the pyrolysis routes and their variants. Conventional pyrolysis is defined as the pyrolysis, which occurs under a slow heating rate. This condition permits the production of solid, liquid, and gaseous pyrolysis products in significant portions. Conventional slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. The heating rate in conventional pyrolysis is typically much slower than that used in fast pyrolysis. A feedstock can be held at constant temperature or slowly heated. Vapors can be continuously removed as they are formed (Mohan et al. 2006). Slow pyrolysis of biomass is associated with high charcoal content, but the fast pyrolysis is associated with

Table 6.5 Pyrolysis routes and their variants

Method	Residence time	Temperature (K)	Heating rate	Products
Carbonation	Few days	675	Very low	Charcoal
Conventional	5–30 min	875	Low	Char, oil, gas
Slow	20–200	900	High	Oil, char, gas
Fast	0.5–5 s	925	Very high	Bio-oil
Flash liquid[a]	<1 s	<925	High	Bio-oil
Flash gas[b]	<1 s	<925	High	Chemicals, gas
Hydropyrolysis[c]	<10 s	<775	High	Bio-oil
Methanopyrolysis[d]	<10 s	>975	High	Chemicals
Ultrapyrolysis[e]	<0.5 s	1275	Very high	Chemicals, gas
Vacuum pyrolysis	2–30 s	675	Medium	Bio-oil

[a] Flash liquid: liquid obtained from flash pyrolysis accomplished in a time of <1 s
[b] Flash gas: gaseous material obtained from flash pyrolysis within a time of <1 s
[c] Hydropyrolysis: pyrolysis with water
[d] Methanopyrolysis: pyrolysis with methanol
[e] Ultrapyrolysis: pyrolysis with very high degradation rate

tar, at low temperature (675–775 K), and/or gas, at high temperature. At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times (Mohan et al. 2006). Flash pyrolysis utilizes a continuous reactor and can convert 70% of the biomass into bio-oil, while the gaseous and char fractions are each composed of 15% of the original biomass. The gaseous and char fractions are generally used to provide heat for the pyrolysis reactor.

Fast pyrolysis (more accurately defined as thermolysis) is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of oxygen. Flash pyrolysis of biomass is the thermochemical process that converts small dried biomass particles into a liquid fuel (bio-oil or biocrude) for almost 75%, and char and non-condensable gases by heating the biomass to 775 K in the absence of oxygen. Char in the vapor phase catalyzes secondary cracking. Table 6.6 shows the range of the main operating parameters for pyrolysis processes.

Table 6.6 Range of the main operating parameters for pyrolysis processes

	Conventional pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis temperature (K)	550–900	850–1250	1050–1300
Heating rate (K/s)	0.01–1	10–200	>1000
Particle size (mm)	5–50	<1	<0.2
Solid residence time (s)	300–3600	0.5–10	<0.5

Design variables required for fast pyrolysis include the following: feed drying, particle size, pretreatment, reactor configuration, heat supply, heat transfer, heating rates, pyrolysis temperature, vapor residence time, secondary cracking, char separation, ash separation, and liquid collection (Mohan et al. 2006).

Vegetable oils can be converted to liquid and gaseous hydrocarbons by pyrolysis, decarboxylation, deoxygenation, and catalytic cracking processes. Vegetable oils from renewable oilseeds can be used when mixed with diesel fuels, and they can also be used as fuels for diesel engines, but their viscosities are much higher than usual diesel fuel and require modifications of the engines. Different ways have been considered to reduce the viscosity of vegetable oils such as dilution, microemulsification, pyrolysis, and transesterification. Compared with transesterification, pyrolysis has more advantages. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel. Sunflower seed oil has been pyrolized to obtain liquid fuels at atmospheric pressure, and a reaction temperature of 560–690 K in the presence of zeolite catalysts. The maximum yields of conversion from pyrolysis of sunflower oil were obtained from 2% zeolite catalytic runs at all temperatures. The yield of conversion then decreased with increasing catalyst percentage. The maximum yield of pyrolysis oil was 54% from 2% zeolite catalytic run at 690 K. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel (Demirbas 2008b).

6.4.2 Reaction Mechanism of Pyrolysis

Earlier kinetic studies have been conducted under a variety of experimental conditions, resulting in conflicting data with a wide range of kinetic parameters (Stamm 1956; Hofmann and Antal 1984; Desrosiers and Lin 1984; Demirbas 1998; Koullas et al. 1998). Thermogravimetric analysis (TGA) is the general approach applied to determine the weight loss of pyrolyzed samples at various reaction temperatures. Comparison of kinetic data from literature is given in Table 6.7.

The pyrolysis process is always initially endothermic, and almost linear in mass loss. At high heating rates, this character is maintained throughout the process. At low heating rates, the well-known exothermic char-forming processes begin at some point to complete with the basic endothermic nature of the process, and drive it back towards thermoneutrality. There is, however, no evidence of thermodynamically different pathways being followed at high and low heating rates, during the initial stages of pyrolysis. This alone does not assure that a change of mechanism does not occur, but there is also no other evidence to suggest such a change in mechanism with heating rate.

It is believed that as the pyrolysis reaction progresses the carbon residue (semichar) becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases (Tran and Charanjit 1978).

The general changes that occur during pyrolysis are below (Babu and Chaurasia 2003; Mohan et al. 2006):

1. Heat transfer from a heat source, to increase the temperature inside the fuel.
2. The initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char.
3. The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel.
4. Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar.
5. Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition.
6. Further thermal decomposition, reforming, water–gas shift reactions, radicals recombination, and dehydrations can also occur, which are a function of the process's residence time/temperature/pressure profile.

A comparison of pyrolysis, ignition, and combustion of coal and biomass particles reveals the following:

1. Pyrolysis starts earlier for biomass compared with coal.
2. The VM content of biomass is higher compared with that of coal.
3. The fractional heat contribution by VM in biomass is on the order of 70% compared with 36% for coal.
4. Biomass char has more O_2 compared with coal. The fractional heat contribution by biomass is on the order of 30% compared with 70% for coal.
5. The heating value of volatiles is lower for biomass compared with that of coal.
6. Pyrolysis of biomass chars mostly releases CO, CO_2, and H_2O.
7. Biomass has ash that is more alkaline in nature, which may aggravate fouling problems.

The organic compounds from biomass pyrolysis are the following groups:

1. A gas fraction containing CO, CO_2, some hydrocarbons and H_2.
2. A condensable fraction containing H_2O and low molecular weight organic compounds (aldehydes, acids, ketones and alcohols).
3. A tar fraction containing higher molecular weight sugar residues, furan derivatives, phenolic compounds and airborne particles of tar and charred material which form the smoke.

Table 6.7 Comparison of kinetic data from literature

Biomass	Frequency factor (min^{-1})	Activation energy (kJ/mole)	Temp. range (K)	Researcher
Douglas fir sawdust	1.1×10^{11}	105	368–525	(Stamm 1956)
Wood	1.4×10^{6}	84.2	>605	(Barooah and Long 1976)
Douglas fir bark	1.3×10^{10}	100–201	450–850	(Tran and Charanjit 1978)
Missouri sawdust	1.9×10^{7}	95.9	565–665	(Koullas et al. 1998)
Hazelnut shell sawdust	4.7×10^{13}	92–170	450–750	(Demirbas 1998)

The mechanism of pyrolysis reactions of biomass was discussed extensively in an earlier study (Demirbas 2000), where the following were discussed: water is formed by dehydration, methanol arises from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials, methanol also arises from methoxyl groups of uronic acid, and acetic acid is formed in the thermal decomposition of all three main components of wood. When the yield of acetic acid originating from the cellulose, hemicelluloses, and lignin is taken into account, the total is considerably less than the yield from the wood itself. Acetic acid also comes from the elimination of acetyl groups originally linked to the xylose unit.

In the pyrolysis processes, furfural is formed by dehydration of the xylose unit. Quantitatively, 1-hydroxy-2-propanone and 1-hydroxy-2-butanone present high concentrations in the liquid products. These two alcohols are partly esterified by acetic acid. In conventional slow pyrolysis, these two products are not found in so great a quantity because of their low stability. If wood is completely pyrolyzed, resulting products are about what would be expected from pyrolyzing the three major components separately. The hemicelluloses would break down first, at temperatures of 470 to 530K. Cellulose follows in the temperature range of 510 to 620K, with lignin being the last component to pyrolyze at temperatures of 550 to 770K. A wide spectrum of organic substances was contained in the pyrolytic liquid fractions given in the literature (Beaumont 1985). Degradation of xylan yields eight main products: water, methanol, formic, acetic and propionic acids, 1-hydroxy-2-propanone, 1-hydroxy-2-butanone and 2-furfuraldeyde. The methoxy phenol concentration decreased with increasing temperature, while phenols and alkylated phenols increased. The formation of both methoxy phenol and acetic acid was possible as a result of the Diels-Alder cycloaddition of a conjugated diene and unsaturated furanone or butyrolactone.

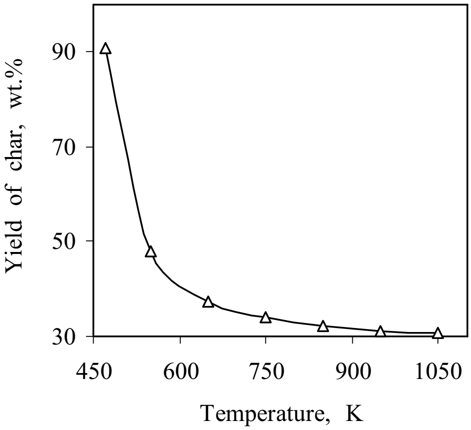
Timell (1967) described the chemical structure of the xylan as the 4-methyl-3-acetylglucoronoxylan. It has been reported that the first runs in the pyrolysis of the pyroligneous acid consist of about 50% methanol, 18% acetone, 7% esters, 6% aldehydes, 0.5% ethyl alcohol, 18.5% water, and small amounts of furfural (Demirbas 2000).

The composition of the water-soluble products was not ascertained but reported to be composed of hydrolysis and oxidation products of glucose such as acetic acid, acetone, simple alcohols, aldehydes, sugars, etc. (Sasaki et al. 1998). Pyroligneous acids disappear in high-temperature pyrolysis. Levoglucosan is also sensitive to heat and decomposes to acetic acid, acetone, phenols, and water.

6.4.3 Char Production

In reference to wood, pyrolysis processes are alternately referred to as carbonization, wood distillation, or destructive distillation processes. Char or charcoal is produced by slow heating wood (carbonization) in airtight ovens or retorts, in chambers with various gases, or in kilns supplied with limited and controlled amounts of air. As generally accepted, carbonization refers to processes in which the char is the prin-

Fig. 6.7 Yield of char from hazelnut shell pyrolysis



cipal product of interest (wood distillation, the liquid; and destructive distillation, both char and liquid). At the usual carbonization temperature of about 675 K, char represents the largest component in wood decomposition products. Typical char from wood contains approximately 80% carbon, 1 to 3% ash, and 12 to 15% volatile components. The char yield decreased gradually from 42.6 to 30.7 % for hazelnut shell and from 35.6 to 22.7% for beech wood with an increase of temperature from 550 to 1150 K, while the char yield from the lignin content decreased sharply from 42.5 to 21.7% until at 850 K during the carbonization procedures. Figure 6.7 shows the yield of char from hazelnut shell pyrolysis (Demirbas 1999). The charcoal yield decreases as the temperature increases. The production of the liquid fraction has a maximum at temperatures between 650 and 750 K. The ignition temperature of charcoal increases as the carbonization temperature increase (Demirbas 2001).

The flow diagram for sustainable char production is presented in Fig. 6.8. Char is manufactured in kilns and retorts. Kilns and retorts generally can be classified as either batch or continuous multiple char manufacturing systems. The continuous multiple systems are more commonly used than are batch systems. Under the sustainable charcoal production, the aim is to minimize material and energy losses at all stages. It is well known that the presence of alkaline cations in biomass affect the mechanism of thermal decomposition during fast pyrolysis causing primarily fragmentation of the monomers making up the natural polymer chains rather than the predominant depolymerization that occurs in their absence.

Wood extractives consist of vegetable oils and valuable chemicals. The vegetable can be converted to biodiesel by transesterification with methanol. The need for increased supplies of charcoal produced from improved and efficient pyrolytic processes is urgent. Recovery of acetic acid and methanol byproducts from pyrolysis was initially responsible for stimulating the charcoal industry. It was shown that hot water washing alone was able to remove a major amount of the alkaline cations (potassium and calcium mainly) from wood (Scott et al. 2000). The wood is then converted into char using improved and efficient kilns after which proper handling is ensured during packaging, storage and transportation to minimize waste. There

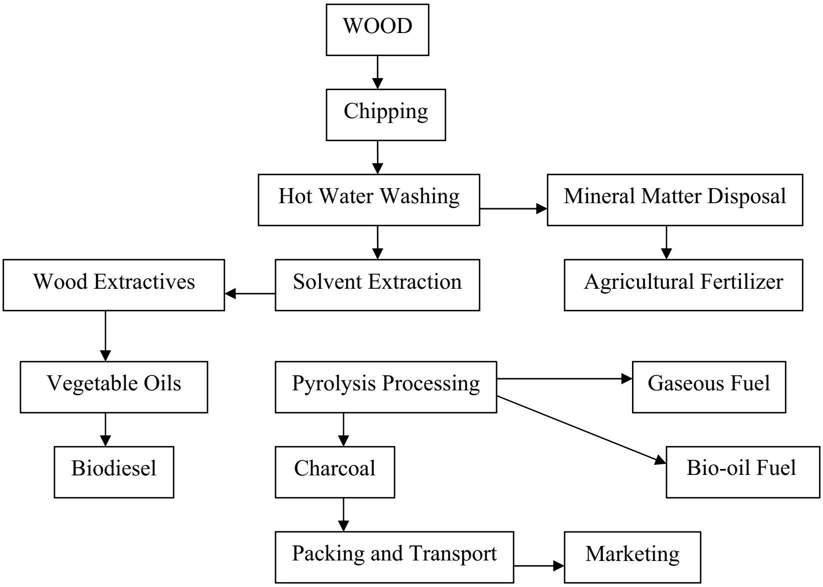


Fig. 6.8 Flow diagram for sustainable char production from wood

are various environmental and socioeconomic benefits associated with each stage in the process.

The elemental composition of char, and its properties, depends on final carbonization temperatures. At increased temperatures, the carbon content increases dramatically. The yield, water absorbency, and hydrogen content decreases rapidly as the carbonization temperature increases. The yield is so low at higher temperatures that the production of charcoal at these temperatures is only of theoretical interest (Demirbas 1999).

Char is very important for developing nations, and for developed ones as well. It is important to learn methods for maximizing its potential, since such a large amount of raw materials are needed for its production. Char is a premium fuel that is widely used in many developing countries to meet household as well as a variety of other needs. It can be readily produced from wood with no capital investment in equipment through the use of charcoal piles, earth kilns, or pit kilns. As the names of these processes suggest, hardwood is carefully stacked in a mound or pit around a central air channel, then covered with dirt, humus, moss, clay, or sod.

6.4.4 Bio-Oil Production

The term bio-oil is used mainly to refer to liquid fuels. Biomass could be converted to liquid, char, and gaseous products via carbonization process at different temperatures. The chemical composition and yields of the char, gas, condensed liquid and tar were determined as function of the carbonization temperature. There are several reasons for bio-oils to be considered as relevant technologies by both developing and industrialized countries: for energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Bio-oils are liquid fuels made from biomass materials, such as agricultural crops, municipal wastes and agricultural and forestry byproducts via biochemical or thermochemical processes. The pyrolysis oil (bio-oil) from wood is typically a liquid, almost black through dark red brown. These liquids have a density of about 1200 kg/m^3, which is higher than that of fuel oil and significantly higher than that of the original biomass. Bio-oils also have water contents of typically 15–30 wt.%, which cannot be removed by conventional methods like distillation. Phase separation may occur above certain water contents. The higher heating value (HHV) is below 27 MJ/kg (compared to 43–46 MJ/kg for conventional fuel oils).

Bio-oils are dark brown, free-flowing organic liquids that are comprised of highly oxygenated compounds. Figure 6.9 shows bio-oil produced from flash pyrolysis. The synonyms for bio-oil include pyrolysis oils, pyrolysis liquids, biocrude oil, wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous acid, and liquid wood. Bio-oils contain many reactive species, which contribute to unusual attributes. Chemically, bio-oil is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics (Demirbas 2007).

For example, the bio-oil formed at 725 K contains high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimetoxyphenol and 2-cyclopenten-1-one, etc. A significant characteristic of the bio-oils was the high percentage of alkylated compounds especially methyl derivatives. As the temperature increased, some of these compounds were transformed via hydrolysis (Kuhlmann et al. 1994). The formation of unsaturated compounds from biomass materials generally involves a variety of reaction pathways such as dehydration, cyclization, Diels-Alder cycloaddition reactions, and ring rearrangement. For example, 2,5-hexandione can undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one with very high selectivity of up to 81% (An et al. 1997).

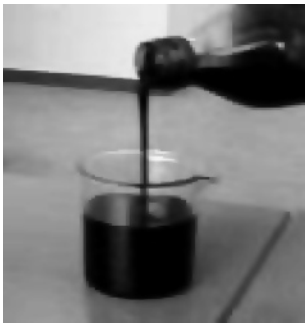


Fig. 6.9 Bio-oil from flash pyrolysis of biomass

The bio-oil produced by flash pyrolysis is a highly oxygenated mixture of carbonyls, carboxyls, phenolics and water. It is acidic and potentially corrosive. Bio-oil can also be potentially upgraded by hydrodeoxygenation. However, there is a severe energy cost in doing this as a result of its high original oxygen content. Fractionation of bio-oil could potentially result in useful chemical and industrial products. The phenolic fraction of bio-oil, derived from lignin in the biomass, makes up approximately 25% of the organics in the bio-oil. This portion has been identified as a potential source of feedstocks for valuable chemicals such as formaldehyde and resins.

Crude bio-oil can potentially be fired in boilers, kilns, engines and turbines. However, the quality of bio-oil produced is a function of the biomass feed source and its use for these purposes must still be proven for a wide range of feedstocks.

The pyrolysis of biomass is a thermal treatment that results in the production of charcoal, liquid, and gaseous products. Among the liquid products, methanol is one of the most valuable products. The liquid fraction of the pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight, and a non-aqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase were higher than those of the non-aqueous phase.

Bio-oil has a higher energy density than biomass, and can be obtained by quick heating of dried biomass in a fluidized bed followed by cooling. The byproduct char and gases can be combusted to heat the reactor. Upgraded bio-oil can be used in engines – either totally or partially in a blend.

Biomass is dried and then converted into bio-oil by very quick exposure to heated particles in a fluidized bed. The char and gases produced are combusted to supply heat to the reactor, while the product oils are cooled and condensed. The bio-oil is then shipped by truck from these locations to the hydrogen production facility. It is more economical to produce bio-oil at remote locations and then ship the oil, since the energy density of bio-oil is higher than biomass. For the following analysis, it was assumed that the bio-oil would be produced at several smaller plants, closer to the sources of biomass, such that more affordable feedstocks can be obtained. The liquid yield from hardwood was reduced to 6.2% at 1150 K. Condensed liquid yield of hardwood showed a maximum peak (40.9%) at 850 K and then decreased to 6.2% at higher temperatures. The tar yield from all biomass samples was at about the same level. Table 6.8 shows the characterization of the chemistry and products from pyrolysis and carbonization processes of biomass (Demirbas 2001).

Typical properties and characteristics of wood-derived bio-oil are presented in Table 6.9 (Demirbas 2001). Bio-oil has many special features and characteristics. These require consideration before any application, storage, transport, upgrading or utilization is attempted.

Table 6.10 shows the fuel properties of diesel fuel and biomass pyrolysis oil. The kinematic viscosity of pyrolysis oil varies from as low as 11 cSt to as high as 115 mm^2/s (measured at 313 K) depending on nature of the feedstock, temperature of pyrolysis process, thermal degradation degree, etc. The pyrolysis oils have water contents of typically 15–30 wt.% of the oil mass, which cannot be removed by conventional methods like distillation. Phase separation may partially occur above

Table 6.8 Characterization of chemistry and products of biomass pyrolysis and carbonization

Type	Feature and process	Products and their characterizations
Pyrolysis of holocellulose	General effects: • Color changes from to brown to black • Flexibility and mechanical strength are lost • Size reduced • Weight reduced	Volatile products: • Readily escape during pyrolysis process • 59 compounds produced of which 37 have been identified • CO, CO_2, H_2O, acetal, furfural, aldehydes, ketones
	Processes:	Tar
	Dehydration • Also known as char forming reactions • Produces volatiles products and char	• Levoglucosan is principal component
	Depolymerization • Produces tar	Chars • As heating continues there is a 80% loss of weight and remaining cellulose is converted to char • Prolonged heating or exposure to higher temperature (900 K) reduces char formation to 9%
	Effect of temperature • At low temperatures dehydration predominates • At 630 K depolymerization with production of levoglucosan dominates • Between 550 and 675 K products formed are independent of temperature	
Pyrolysis of lignin	Conventional (carbonization): • At 375–450 K endotherm • At 675 K exotherm • Maximum rate occurring between 625 and 725 K	Char approximately 55%: Distillates (20%) • Methanol – methoxyl groups, acetic acid, acetone Tar (15%) • Phenolic compounds and carboxylic acid Gases • CO, methane, CO_2, ethane
	Fast and flash pyrolysis: • High temperature of 750 K • Rapid heating rate • Finely ground feed material • Less than 10% MC • Rapid cooling and condensation of gases • Yields in 80% range • Char and gas used for fuel	Bio-oil: • Will not mix with hydrocarbon liquids • Cannot be distilled • Substitute for fuel oil and diesel in boilers, furnaces, engines, turbines, etc. Phenol • Utilizes a solvent extraction process to recover phenolics and neutrals • 18–20% of wood weight • Secondary processing of phenol formaldehyde resins • Adhesives • Injected molded plastics

Table 6.8 (*continued*) Characterization of chemistry and products of biomass pyrolysis and carbonization

Type	Feature and process	Products and their characterizations
Pyrolysis of lignin		Other chemicals • Extraction process • Chemical for stabilizing the brightness regression of thermochemical pulp (TMP) when exposed to light • Food flavorings, resins, fertilizers, etc.

Table 6.9 Typical properties and characteristics of wood-derived bio-oil

Property	Characteristics
Appearance	From almost black or dark red-brown to dark green, depending on the initial feedstock and the mode of fast pyrolysis.
Miscibility	Varying quantities of water exist, ranging from ~15 wt.% to an upper limit of ~30–50 wt.% water, depending on production and collection. Pyrolysis liquids can tolerate the addition of some water before phase separation occurs. Bio-oil cannot be dissolved in water. Miscible with polar solvents such as methanol, acetone, etc., but totally immiscible with petroleum-derived fuels.
Density	Bio-oil density is ~1.2 kg/L, compared to ~0.85 kg/L for light fuel oil.
Viscosity	Viscosity of bio-oil varies from as low as 25 cSt to as high as 1000 cSt (measured at 313 K) depending on the feedstock, the water content of the oil, the amount of light ends that have collected, the pyrolysis process used, and the extent to which the oil has been aged.
Distillation	It cannot be completely vaporized after initial condensation from the vapor phase at 373 K or more, it rapidly reacts and eventually produces a solid residue from ~50 wt.% of the original liquid. It is chemically unstable, and the instability increases with heating. It is always preferable to store the liquid at or below room temperature; changes do occur at room temperature, but much more slowly and they can be accommodated in a commercial application.
Ageing of pyrolysis liquid	Causes unusual time-dependent behavior. Properties such as viscosity increases, volatility decreases, phase separation, and deposition of gums change with time.

certain water contents. The water content of pyrolysis oils contributes to their low energy density, lowers the flame temperature of the oils, leads to ignition difficulties, and, when preheating the oil, can lead to premature evaporation of the oil and resultant injection difficulties. The higher heating value (HHV) of pyrolysis oils is below 26 MJ/kg (compared to 42–45 MJ/kg for conventional petroleum fuel oils). In contrast to petroleum oils, which are non-polar and in which water is insoluble,

Table 6.10 Fuel properties of diesel, biodiesel and biomass pyrolysis oil

Property	Test method	ASTM D975 (diesel)	ASTM D6751 (biodiesel, B100)	Pyrolysis oil (bio-oil)
Flash point	D 93	325 K min	403 K	–
Water and sediment	D 2709	0.05 Max vol.%	0.05 Max vol.%	0.01–0.04
Kinematic viscosity (at 313 K)	D 445	1.3–4.1 mm²/s	1.9–6.0 mm²/s	25–1000
Sulfated ash	D 874	–	0.02 Max wt.%	–
Ash	D 482	0.01 Max wt.%	–	0.05–0.01 wt.%
Sulfur	D 5453	0.05 Max wt.%	–	–
Sulfur	D 2622/129	–	0.05 Max wt.%	0.001–0.02 wt.%
Copper strip corrosion	D 130	No. 3 max	No. 3 max	–
Cetane number	D 613	40 min	47 min	–
Aromaticity	D 1319	–	35 Max vol.%	–
Carbon residue	D 4530	–	0.05 Max mass%	0.001–0.02 wt.%
Carbon residue	D 524	0.35 Max mass%	–	–
Distillation temperature	D 1160	555 K min –611 K max	–	–

biomass oils are highly polar and can readily absorb over 35% water (Demirbas 2007).

Figure 6.10 shows the fractionation of biomass pyrolysis products. The liquid from pyrolysis is often called oil, but is more like tar. This also can be degraded to liquid hydrocarbon fuels. The crude pyrolysis liquid is a thick black tarry fluid. The tar is a viscous black fluid that is a byproduct of the pyrolysis of biomass and is used in pitch, varnishes, cements, preservatives, and medicines as disinfectants and anti-septics. Chemical and physical properties for bio-oils and fuels are given in Table 6.11.

The gas product from pyrolysis usually has a medium heating value (MHV) fuel gas around 15–22 MJ/NM³ or a lower heating value (LHV) fuel gas of around 4–8 MJ/Nm³ from partial gasification depending on feed and processing parameters.

6.4.5 Chemicals and Fuels Production

Table 6.12 shows the gas chromatographic analysis of bio-oil from beech wood pyrolysis (Demirbas 2007). The bio-oil formed at 725 K contained high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-

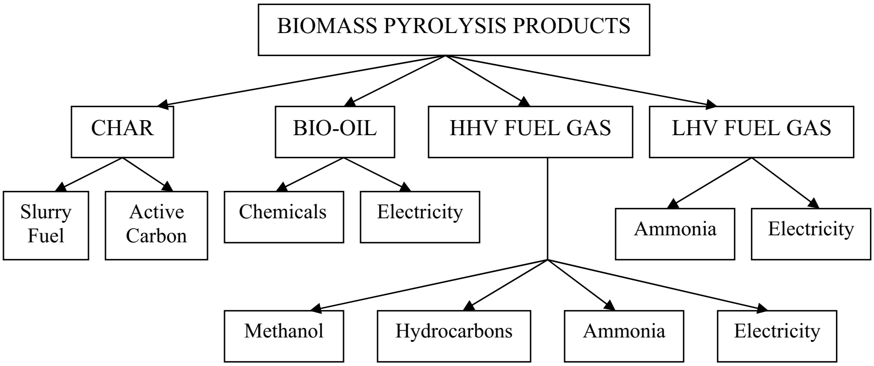


Fig. 6.10 Fractionation of biomass pyrolysis products

Table 6.11 Chemical and physical properties of biomass bio-oils and fuel oils

	Pine	Oak	Poplar	Hardwood	No. 2 oil	No. 6 oil
Elemental (wt.% dry)						
C	56.3	55.6	59.3	58.8	87.3	87.7
H	6.5	5.0	6.6	9.7	12.0	10.3
O (by different)	36.9	39.2	33.8	31.2	0.0	1.2
N	0.3	0.1	0.2	0.2	<0.01	0.5
S	–	0.0	0.00	0.04	0.1	0.8
Proximate (wt.%)						
Ash	0.05	0.05	<0.001	0.07	<0.001	0.07
Water	18.5	16.1	27.2	18.1	0.0	2.3
Volatiles	66.0	69.8	67.4	–	99.8	94.1
Fixed C (by different)	15.5	14.1	5.4	–	0.1	3.6
Viscosity (mm^2/s) at 313 K	44	115	11	58	2.6	–
Density (kg/m^3) at 313 K	1210	1230	–	1170	860	950
Pyrolysis yield (wt.%)						
Dry oil	58.9	55.3	41.0	–	–	–
Water	13.4	10.4	14.6	–	–	–
Char	19.6	12.2	16.4	–	–	–
Gases	13.9	12.4	21.7	–	–	–

propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimetoxyphenol and 2-cyclopenten-1-one, etc. A significant characteristic of the bio-oils was the high percentage of alkylated compounds, especially methyl derivatives.

Table 6.12 Gas chromatographic analysis of bio-oil from beech wood pyrolysis (wt.% dry basis)

Compound	Reaction temperature (K)					
	625	675	725	775	825	875
Acetic acid	16.80	16.5	15.9	12.6	8.42	5.30
Methyl acetate	0.47	0.35	0.21	0.16	0.14	0.11
1-Hydroxy-2-propanone	6.32	6.84	7.26	7.66	8.21	8.46
Methanol	4.16	4.63	5.08	5.34	5.63	5.82
1-Hydroxy-2-butanone	3.40	3.62	3.82	3.88	3.96	4.11
1-Hydroxy-2-propane acetate	1.06	0.97	0.88	0.83	0.78	0.75
Levoglucosan	2.59	2.10	1.62	1.30	1.09	0.38
1-Hydroxy-2-butanone acetate	0.97	0.78	0.62	0.54	0.48	0.45
Formic acid	1.18	1.04	0.84	0.72	0.60	0.48
Guaiacol	0.74	0.78	0.82	0.86	0.89	0.93
Crotonic acid	0.96	0.74	0.62	0.41	0.30	0.18
Butyrolactone	0.74	0.68	0.66	0.67	0.62	0.63
Propionic acid	0.96	0.81	0.60	0.49	0.41	0.34
Acetone	0.62	0.78	0.93	1.08	1.22	1.28
2,3-Butanedione	0.46	0.50	0.56	0.56	0.58	0.61
2,3-Pentanedione	0.34	0.42	0.50	0.53	0.59	0.64
Valeric acid	0.72	0.62	0.55	0.46	0.38	0.30
Iso-valeric acid	0.68	0.59	0.51	0.42	0.35	0.26
Furfural	2.52	2.26	2.09	1.84	1.72	1.58
5-Methyl-furfural	0.65	0.51	0.42	0.44	0.40	0.36
Butyric acid	0.56	0.50	0.46	0.39	0.31	0.23
Iso-butyric acid	0.49	0.44	0.38	0.30	0.25	0.18
Valerolactone	0.51	0.45	0.38	0.32	0.34	0.35
Propanone	0.41	0.35	0.28	0.25	0.26	0.21
2-Butanone	0.18	0.17	0.32	0.38	0.45	0.43
Crotonolactone	0.12	0.19	0.29	0.36	0.40	0.44
Acrylic acid	0.44	0.39	0.33	0.25	0.19	0.15
2-Cyclopenten-1-one	1.48	1.65	1.86	1.96	2.05	2.13
2-Methyl-2-cyclopenten-1-one	0.40	0.31	0.24	0.17	0.13	0.14
2-Methyl-cyclopentenone	0.20	0.18	0.17	0.22	0.25	0.29
Cyclopentenone	0.10	0.14	0.16	0.23	0.27	0.31
Methyl-2-furancarboxaldehyde	0.73	0.65	0.58	0.50	0.44	0.38
Phenol	0.24	0.30	0.36	0.43	0.54	0.66
2,6-Dimethoxyphenol	2.28	2.09	1.98	1.88	1.81	1.76

Table 6.12 (*continued*) Gas chromatographic analysis of bio-oil from beech wood pyrolysis (wt.% dry basis)

Compound	Reaction temperature (K)					
	625	675	725	775	825	875
Dimethyl phenol	0.08	0.13	0.18	0.42	0.64	0.90
Methyl phenol	0.32	0.38	0.44	0.50	0.66	0.87
4-Methyl-2,6-dimetoxyphenol	2.24	2.05	1.84	1.74	1.69	1.58

The influence of temperature on the compounds in liquid products obtained from biomass samples via pyrolysis were examined in relation to the yield and composition of the product bio-oils. The product liquids were analyzed by a gas chromatography-mass spectrometry combined system. The bio-oils were composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaiacol and their alkylated phenol derivatives. Thermal depolymerization and decomposition of biomass structural components, such as cellulose, hemicelluloses, and lignin form liquids and gas products, as well as a solid residue of charcoal. The structural components of the biomass samples mainly affect the pyrolytic degradation products.

The supercritical water extraction and liquefaction partial reactions also occur during the pyrolysis. Acetic acid is formed in the thermal decomposition of all three main components of biomass. In the pyrolysis reactions of biomass many processes occur: water is formed by dehydration, acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit, furfural is formed by dehydration of the xylose unit, formic acid proceeds from carboxylic groups of uronic acid, and methanol arises from methoxyl groups of uronic acid (Demirbas 2007).

Chemical groups obtained from biomass bio-oil by fast pyrolysis are acids, aldehydes, alcohols, sugars, esters, ketones, phenolics, oxygenates, hydrocarbons, and steroids, shown in Table 6.13.

Table 6.13 Chemicals from biomass bio-oil by fast pyrolysis

Chemical	Minimum (wt.%)	Maximum (wt.%)
Levoglucosan	2.9	30.5
Hydroxyacetaldehyde	2.5	17.5
Acetic acid	6.5	17.0
Formic acid	1.0	9.0
Acetaldehyde	0.5	8.5
Furfuryl alcohol	0.7	5.5
1-Hydroxy-2-propanone	1.5	5.3
Catechol	0.5	5.0

Table 6.13 (*continued*) Chemicals from biomass bio-oil by fast pyrolysis

Chemical	Minimum (wt.%)	Maximum (wt.%)
Methanol	1.2	4.5
Methyl glyoxal	0.6	4.0
Ethanol	0.5	3.5
Cellobiosan	0.4	3.3
1,6-Anhydroglucofuranose	0.7	3.2
Furfural	1.5	3.0
Fructose	0.7	2.9
Glyoxal	0.6	2.8
Formaldehyde	0.4	2.4
4-Methyl-2,6-dimetoxyphenol	0.5	2.3
Phenol	0.2	2.1
Propionic acid	0.3	2.0
Acetone	0.4	2.0
Methylcyclopentene-ol-one	0.3	1.9
Methyl formate	0.2	1.9
Hydroquinone	0.3	1.9
Acetol	0.2	1.7
2-Cyclopenten-1-one	0.3	1.5
Syringaldehyde	0.1	1.5
1-Hydroxy-2-butanone	0.3	1.3
3-Ethylphenol	0.2	1.3
Guaiacol	0.2	1.1

Figure 6.11 shows the vegetable oil upgrading processes. Palm oil has been cracked at atmospheric pressure and a reaction temperature of 723 K to produce bio-oil in a fixed-bed microreactor. The reaction was carried out over microporous HZSM-5 zeolite, mesoporous MCM-41, and composite micromesoporous zeolite as catalysts. The products obtained were gas, liquid (bio-oil), water, and coke. The bio-oil product was composed of hydrocarbons corresponding to gasoline, kerosene, and diesel boiling point range. The maximum conversion of palm oil, 99 wt.%, and gasoline yield of 48 wt.% was obtained with composite micromesoporous zeolite (Sang 2003). The gasoline yield increased with the increase in the Si/Al ratio due to the decrease in the secondary cracking reactions and the drop in the yield of gaseous products. The vegetable oils could be converted to liquid products containing gasoline boiling range hydrocarbons. The results show that the product compositions are affected by catalyst content and temperature.

There are two ethanol production processes that currently employ thermochemical reactions in their processes. The first system is actually a hybrid thermochemi-

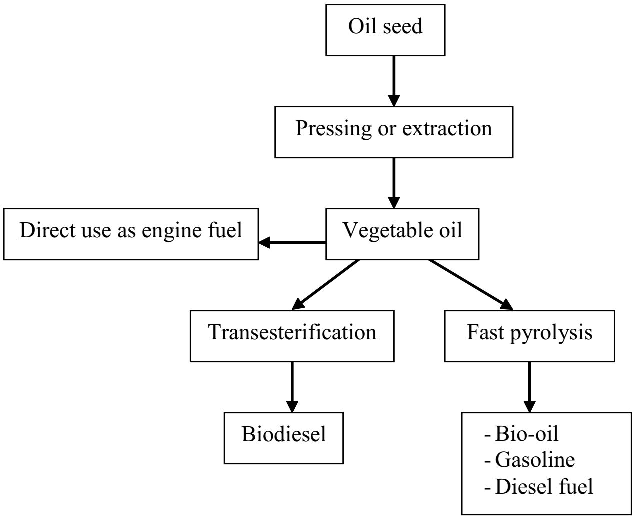


Fig. 6.11 Vegetable oil upgrading processes

cal and biological system. Lignocellulosic biomass materials are first thermochemically gasified and the synthesis gas (a mixture of hydrogen and carbon monoxide) is bubbled through specially designed fermenters. The biomass gasification reaction is:

$$C + H_2O \rightarrow CO + H_2 \tag{6.4}$$

A microorganism that is capable of converting the synthesis gas is introduced into the fermenters under specific process conditions to cause fermentation to bioethanol.

The second thermochemical ethanol production process does not use any microorganisms. In this process, biomass materials are first thermochemically gasified and the synthesis gas passed through a reactor containing catalysts, which cause the gas to be converted into ethanol. Numerous efforts have been made since then to develop commercially viable thermochemical-to-ethanol processes. Ethanol yields up to 50% have been obtained using synthesis gas-to-ethanol processes. Some processes that first produce methanol and then use catalytic shifts to produce ethanol have obtained ethanol yields in the range of 80%. Unfortunately, like the other processes, finding a cost-effective all-thermochemical process has been difficult.

6.4.6 *Upgrading of Pyrolysis Products*

The overview of a fast pyrolysis liquids-based biorefinery is given in Fig. 6.12. Biorefineries for the purpose of producing several products and byproducts such as biofuels, heat and/or electricity, have been in focus in the recent years. In a biore-

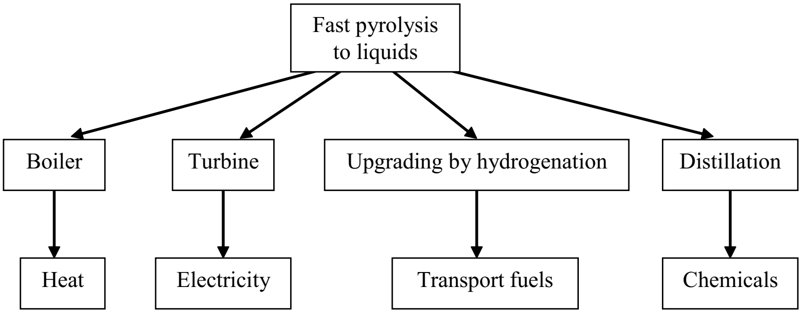


Fig. 6.12 Overview of fast pyrolysis liquids-based biorefinery

finery, biomass can be converted to useful biomaterials and/or energy carriers in an integrated manner and thereby maximize the economic value of the biomass used while reducing the waste streams produced (Zhang 2008).

Figure 6.13 shows biomass upgrading by pyrolysis. Upgrading of condense liquid from biomass includes three stages: physical upgrading (differential condensation, liquid filtration and solvent addition), catalytic upgrading (deoxygenating and reforming), and chemical upgrading (new fuel and chemicals synthesis).

The bio-oil obtained from the fast pyrolysis of biomass has a high oxygen content. Ketones and aldehydes, carboxylic acids and esters, aliphatic and aromatic alcohols, and ethers have been detected in significant quantities. Because of the reactivity of oxygenated groups, the main problems of the oil are instability. Therefore study of the deoxygenation of bio-oil is needed. In the previous work the mechanism of hydrodeoxygenation (HDO) of bio-oil in the presence of a cobalt molybdate catalyst was studied (Zhang et al. 2003).

The main hydrodeoxygenation (HDO) reaction is represented in Eq. 6.5:

$$-(CH_2O)- + H_2 \rightarrow -(CH_2)- + H_2O \tag{6.5}$$

This is the most important route of chemical upgrading. The reaction in Eq. 6.5 is analogous to typical refinery hydrogenations like hydrodesulfurization and hydrodenitrification. In general, most of the hydrodeoxygenation studies have been performed using existing hydrodesulfurization catalysts (NiMo and CoMo on suitable carriers). Such catalysts need activation using a suitable sulfur source and this is a major drawback when using nearly sulfur-free resources like bio-oil. Table 6.14 shows the upgrading processes of flash pyrolysis liquid or bio-oil.

Hydroprocessing is the term used for the catalytic reactions of hydrogen with process streams to remove the heteroatoms sulfur, nitrogen, oxygen, and metals, and for the saturation of aromatic structures. Hydroprocessing can also refer to hydrogenation of olefins or other unsaturated species. Hydroprocessing is carried out in fixed-bed reactors at high pressures, with severe reaction conditions generally increasing with the heaviness of the feed. Reactors used with the heavier feeds are trickle beds, in which the liquid oil trickles through the catalyst bed, with hydrogen concentrated in the gas phase. Slurry reactors have also been used for heavy feedstocks.

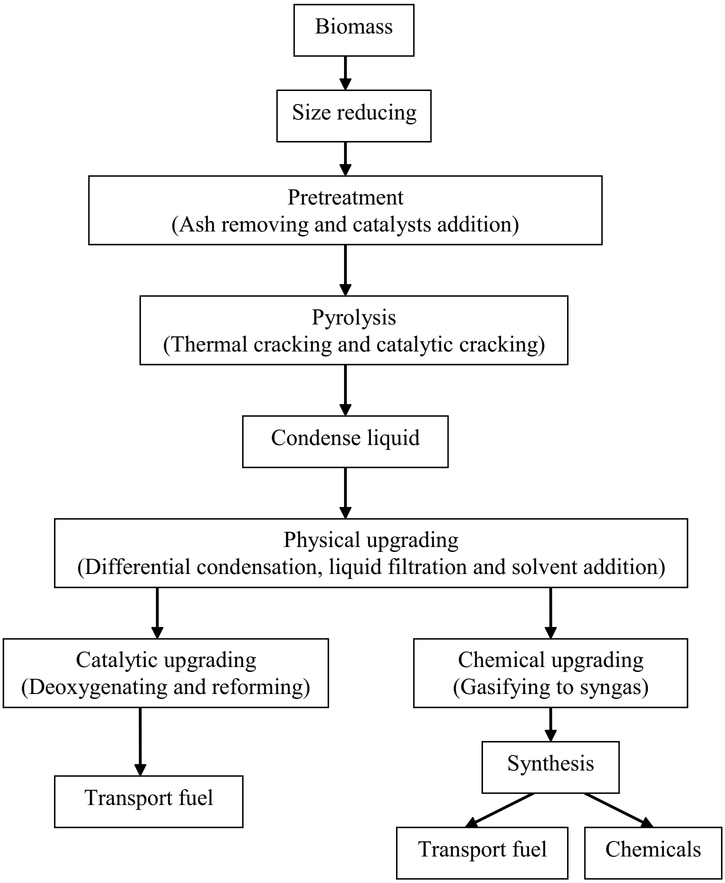


Fig. 6.13 Biomass upgrading by pyrolysis

Table 6.14 Upgrading processes of flash pyrolysis liquid or bio-oil

Upgrading process	Products
Hydrodeoxygenation (HDO)	Fuel, chemicals (phenolics)
Homogenous catalyst hydrogenation	Stabilized oil
Alcoholysis and reactive distillation	Fuel
Reactive extraction	Chemicals (organic acids)

The primary objective, catalytic partial hydrodeoxygenation, is to increase the energetic value of the oil by removing bound oxygen in the form of water. Hydrodeoxygenation of bio-oils involves treating the oils at moderate temperatures with high-pressure hydrogen in the presence of heterogeneous catalysts. The process was carried out in two distinct stages, a first stage at relatively low temperatures (525–575 K), aimed to stabilize the bio-oil and a second stage at higher tempera-

Table 6.15 Properties of the raw and upgraded bio-oil

Property	Raw bio-oil	Upgraded bio-oil
Density (kg/L)	1.12	0.93
Elemental analysis (wt.%)		
C	60.4	87.7
H	6.9	8.9
O	41.8	3.0
N	0.9	0.4
Higher heating value (MJ/kg)	21.3	41.4

tures (575–675 K) to deoxygenate the intermediate product. Different types of catalysts were screened, ranging from conventional sulfided catalysts used in the HDS process (i. e., NiMo/Al_2O_3, CoMo/Al_2O_3) to novel non-sulfided catalysts based on noble metal catalysts (i. e., Ru/Al_2O_3). Operating conditions were optimized to obtain the highest yield of a hydrocarbon like liquid product.

Hydrogen can be used to convert biomass to fuels, which requires a higher level of hydrodeoxygenation compared to the conversion of fossil feedstocks to fuels. “Green diesel” refers to an acceptable diesel pool blend component produced from a suitable biofeedstock. Green diesel can be produced by either hydrodeoxygenation or decarboxylation of plant oils and greases with propane as a co-product. Although hydrodeoxygenation removes oxygen from a triglyceride or free fatty acid by reaction with hydrogen to form water and an *n*-paraffin, decarboxylation removes oxygen in the biomass carboxy groups to form carbon dioxide and a shorter *n*-paraffin (Kaparaju et al. 2009).

Properties of the raw and upgraded bio-oil are given in Table 6.15. As seen in this table, properties of the raw and upgraded bio-oil are highly different.

6.4.7 Refining of Pyrolysis Products

Various aspects of biorefinery research and development since the beginning of the 1990s are presented. Many of the currently used biorenewable-based industry products are results of direct physical, catalytical or chemical treatment and processing of biomass feedstocks.

The primary objective is the refining of pyrolysis products to obtain valuable fuels like gasoline, diesel fuel and jet fuel, and chemicals from biomass. Figure 6.14 shows the products from biomass by pyrolysis-based refinery.

In vacuum pyrolysis, biomass is heated in a vacuum in order to decrease the boiling point and avoid adverse chemical reactions. In flash vacuum thermolysis (FVT), the residence time of the substrate at the working temperature is limited as much as possible, again in order to minimize secondary reactions. Figure 6.15 shows the multiple stages vacuum pyrolysis of biomass.

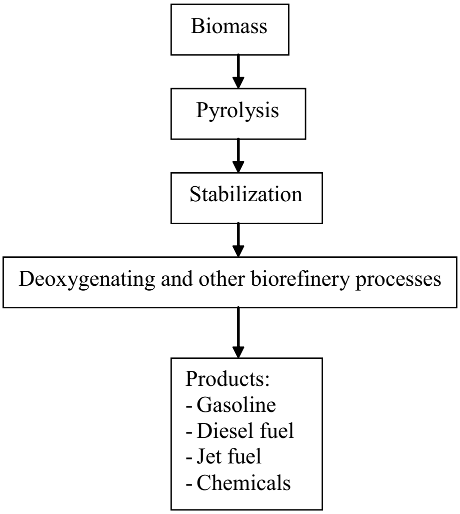


Fig. 6.14 Products from biomass by pyrolysis-based refinery

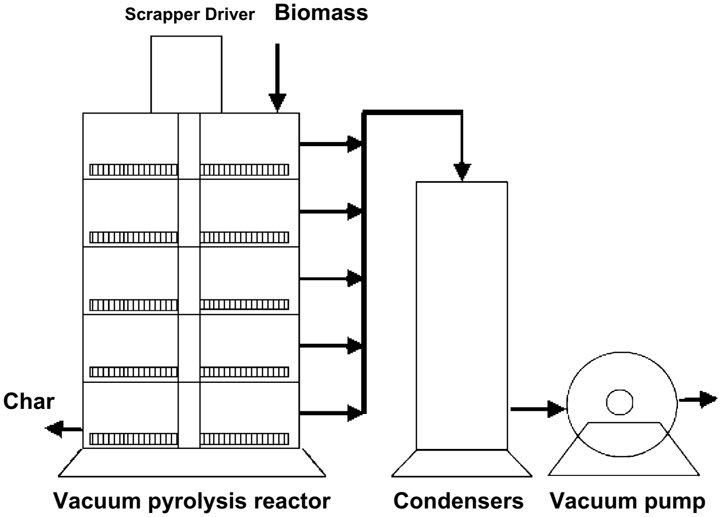


Fig. 6.15 Multiple stages vacuum pyrolysis of biomass

Vacuum pyrolysis is the thermal degradation of a feedstock in the absence of oxygen and under low pressure, to produce a bio-oil and char as main products, together with water and non-condensable gases. Both the bio-oil and char have a high-energy content and may be used as fuels. An incredible number of chemical compounds are also found in the bio-oil and these compounds can be extracted and sold as high-value chemicals.

Vacuum pyrolysis is a relatively new variant of pyrolysis with many recycling applications. During vacuum pyrolysis of biomass, the biorenewable feedstock is thermally decomposed under reduced pressure. The quick removal of the vapors reduces the residence times of the macromolecules and hence minimizes secondary

Table 6.16 Comparison of pyrolysis and gasification processes

Process	Conditions	Products (wt.%)		
		Liquid	Char	Gas
Fast pyrolysis	Moderate temperature (700–800 K) Short hot vapor residence time (< 2 s)	70–77	10–14	11–15
Slow pyrolysis	Low-moderate temperature (600–725 K) Long residence time	27–33	33–38	33–38
Vacuum pyrolysis	Moderate temperature (675 and 775 K) Low pressure (< 0.15 atm)	74–80	8–12	9–14
Gasification	High temperature (> 1075 K) Long residence time	4–6	8–12	82–88

decomposition reactions such as cracking, repolymerization and recondensation, which occur during atmospheric pyrolysis. Temperatures between 675 and 775 K and pressures of about 0.15 atmospheres are typically used. Table 6.16 gives a comparison of pyrolysis and gasification processes.

6.4.8 Refining Opportunities for Bio-Oil

The bio-oil contains the thermally cracked products of the original cellulose, hemicelluloses, and lignin fractions present in the biomass. It also contains a high percentage of water, often as high as 30%. The total oil is often homogeneous after quenching but can easily be separated into two fractions: a water-soluble fraction and a heavier pyrolytic lignin fraction. The addition of more water allows the pyrolytic lignin fraction to be isolated and the majority of it consists of the same phenolic polymer as lignin but with smaller molecular weight fragments. Pyrolytic lignin is a better feedstock for liquid fuel production than the water-soluble fraction because of its lower oxygen content and therefore the study focused on evaluating it as a potential feedstock for the production of highly aromatic gasoline.

6.5 Gasification Process

Gasification is a form of pyrolysis, carried out at high temperatures in order to optimize the gas production. The resulting gas, known as producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. Gasification of biomass is a well-known technology that can be classified depending on the gasifying agent: air, steam, steam-oxygen, air-steam, O_2-enriched air, etc.

Biomass gasification technologies have historically been based upon partial oxidation or partial combustion principles, resulting in the production of a hot, dirty,

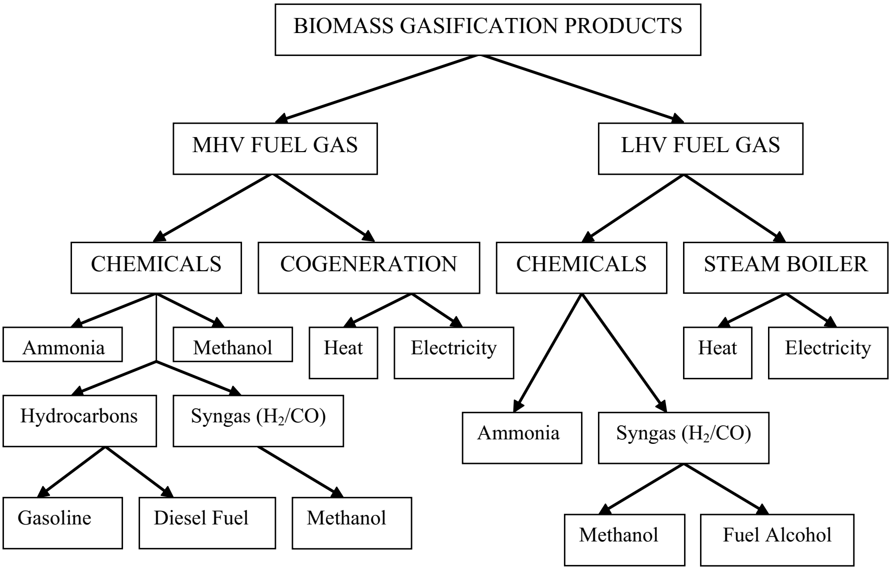


Fig. 6.16 Fractionation of biomass gasification products

low heating value gas that must be directly ducted into boilers or dryers. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy.

Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. These processes suffer from low thermal efficiencies and low calorific gas because of the energy required to evaporate the moisture typically inherent in the biomass and the oxidation of a portion of the feedstock to produce this energy. In gasification, the aim is to convert biomass entirely into the gas phase. Either the fuel is partially oxidized directly to produce the heat, or heat is provided indirectly in conjunction with direct steam injection to drive its decomposition to gaseous fuel products such as carbon monoxide, hydrogen, methane and some higher weight hydrocarbons, collectively referred to as tars. If air or oxygen is used directly in the gasifier, generally only about 30% of the stoichiometric oxygen required for full oxidation is supplied to a gasifier. As a result of this oxidation, the gaseous product also contains the non-fuel components carbon dioxide, water and, if air is used, nitrogen. Potential biomass fuel sources for gasification are quite abundant. One of the great advantages of gasification is its ability to process rather diverse and heterogeneous feedstocks. Moisture content is the most critical raw fuel parameter to ensure a higher-quality product gas.

Figure 6.16 shows the fractionation of biomass gasification products. The biomass fuels are suitable for the highly efficient power generation cycles based on gasification and pyrolysis processes. A product gas from thermal decomposition is composed of CO, CO_2, H_2O, H_2, CH_4, other gaseous hydrocarbons (CHs), tars, char, inorganic constituents, and ash. Gas composition of product from the biomass gasification depends heavily on the gasification process, the gasifying agent, and the feedstock composition. The relative amount of CO, CO_2, H_2O, H_2, and (CHs) depends on the stoichiometry of the gasification process. If air is used as the gasifying agent, then roughly half of the product gas is N_2. The air/fuel ratio in a gasification process generally ranges from 0.2 to 0.35 and if steam is the gasifying agent, the steam/biomass ratio is around 1. The actual amount of CO, CO_2, H_2O, H_2, tars, and (CHs) depends on the partial oxidation of the volatile products, as shown in Eq. 6.6:

$$C_nH_m + (n/2+m/4)\ O_2 \leftrightarrows nCO + (m/2)\ H_2O \tag{6.6}$$

The major thermochemical reactions include the following:

Steam and methane:

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \tag{6.7}$$

Water–gas shift:

$$CO + H_2O \leftrightarrows CO_2 + H_2 \tag{6.8}$$

Carbon char to methane:

$$C + 2H_2 \leftrightarrows CH_4 \tag{6.9}$$

Carbon char oxides (Boudouard reaction):

$$C + CO_2 \leftrightarrows 2CO \tag{6.10}$$

6.5.1 Gasification Facilities

The relative simplicity of the gasification system enables its operation to be within the technical expertise of most operators who are experienced with conventional boilers and furnaces, and results in favorable project economics. Its modular design allows a wide range of scale-up or scale-down possibilities, so the systems can vary in size from about one ton per hour of residue to 20 tons per hour or larger, with the size being limited only by biomass availability.

The main steps in the gasification process are:

- Step 1. Biomass is delivered to a metering bin from which it is conveyed with recycled syngas or steam, without air or oxygen into the gasifier.
- Step 2. The material is reformed into a hot syngas that contains the inorganic (ash) fraction of the biomass and a small amount of unreformed carbon.
- Step 3. The sensible heat in the hot syngas is recovered to produce heat for the reforming process.
- Step 4. The cool syngas passes through a filter and the particulate in the syngas is removed as a dry, innocuous waste. The clean syngas is then available for combustion in engines, turbines, or standard natural gas burners with minor modifications.

For electricity generation, the two most competitive technologies are direct combustion and gasification. Typical plant sizes at present range from 0.1 to 50 MW. Co-generation applications are very efficient and economical. Fluidized bed com-

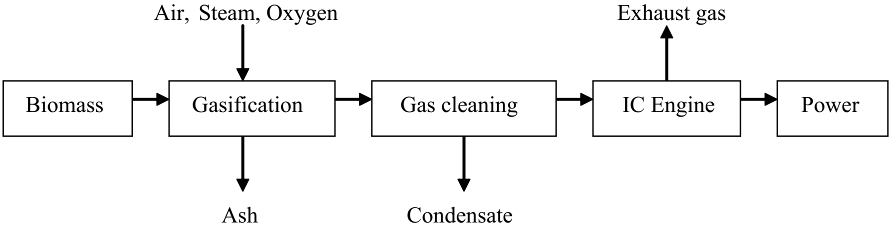


Fig. 6.17 System for power production by means of biomass gasification

bustion (FBC) is efficient and flexible in accepting varied types of fuels. Gasifiers first convert solid biomass into gaseous fuels, which is then used through a steam cycle or directly through gas turbine/engine. Gas turbines are commercially available in sizes ranging from 20 to 50 MW (Badin and Kirschner 1998).

Commercial gasifiers are available in a range of size and types, and run on a variety of fuels, including wood, charcoal, coconut shells and rice husks. Power output is determined by the economic supply of biomass, which is limited to 80 MW in most regions (Overend 1998). Figure 6.17 shows the system for power production by means of biomass gasification. The gasification system of biomass in fixed-bed reactors provides the possibility of combined heat and power production in the power range of 100 kWe up to 5 MWe. A system for power production by means of fixed-bed gasification of biomass consists of the main unit gasifier, the gas cleaning system, and engine.

Gasifiers are used to convert biomass into a combustible gas. The combustible gas is then used to drive a high efficiency, combined-cycle gas turbine. Combustible gas energy conversion devices that are discussed are reciprocating engines, turbines, microturbines, fuel cells, and anaerobic digesters. The resulting combustible gas can be burnt to provide energy for cooking and space heating, or create electricity to power other equipment. Since many of the parasites and disease-producing organisms in the waste are killed by the relatively high temperature in the digester tanks, the digested material can also be used as fertilizer or fish feed.

Various gasification technologies include gasifiers where the biomass is introduced at the top of the reactor and the gasifying medium is either directed co-currently (downdraft) or counter-currently up through the packed bed (updraft). Other gasifier designs incorporate circulating or bubbling fluidized beds. Table 6.17 shows the fixed-bed and fluidized-bed gasifiers and reactor types used in gasification pro-

Table 6.17 Fixed-bed and fluidized-bed gasifiers and reactor types using in gasification processes

Gasifier	Reactor type
Fixed bed	Downdraft, updraft, co-current, counter-current, cross-current, others
Fluidized bed	Single reactor, fast fluid bed, circulating bed

Table 6.18 Composition of gaseous products from various biomass fuels by different gasification methods (% by volume)

H_2	CO_2	O_2	CH_4	CO	N_2
10–19	10–15	0.4–1.5	1–7	15–30	43–60

cesses. Table 6.18 shows composition of gaseous products from various biomass fuels by different gasification methods.

Numerous types of gasifiers have been developed and tested and many industrial applications can use the technology. Gasifiers have been built and operated using a wide variety of configurations including:

1. Fixed-bed (updraft or downdraft fixed beds) gasifiers
2. Fluidized-bed (fluidized or entrained solids serve as the bed material) gasifiers
3. Others including moving grate beds and molten salt reactors

Schematic diagrams of updraft (counter-current) and downdraft (co-current) fixed-bed gasifiers are shown in Figs. 6.18 and 6.19, respectively. Other gasifier designs incorporate circulating or bubbling fluidized beds.

In the drying zone, feedstock descends into the gasifier and moisture is removed using the heat generated in the zones below by evaporation. In the distillation zone, pyrolysis and partial oxidation takes place using the thermal energy released by the partial oxidation of the pyrolysis products. Tar yields can range from 0.1% (down-

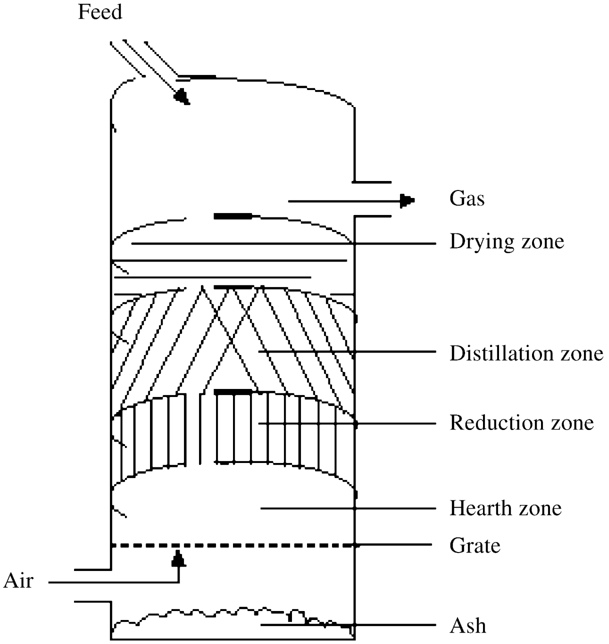


Fig. 6.18 Schematic diagram of an updraft fixed-bed gasifier

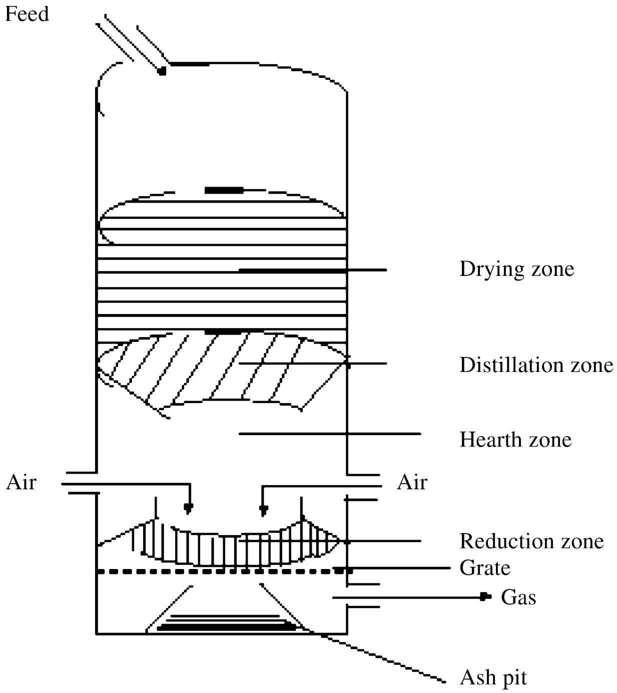


Fig. 6.19 Schematic diagram of a downdraft fixed-bed gasifier

draft) to 20% (updraft) or greater in the product gases. The oxidation reactions of the volatiles are very rapid and the oxygen is consumed before it can diffuse to the surface of the char. In the reduction zone (often referred to as the gasification zone) the char is converted into product gas by reaction with the hot gases from the upper zones. Depending on the end use, it is necessary to cool and clean the gas in order to remove as much water vapor, dust and pyrolytic products as possible from the gas, especially if it is to be used in an internal combustion engine.

Fixed-bed gasifiers are the most suitable for biomass gasification. Fixed-bed gasifiers are usually fed from the top of the reactor and can be designed in either updraft or downdraft configurations. The product gases from these two gasifier configurations vary significantly. At larger scales, fixed-bed gasifiers can encounter problems with bridging of the biomass feedstock. This leads to uneven gas flow. Achieving uniform temperatures throughout the gasifier on large scales can also be difficult due to the absence of mixing in the reaction zone. Most fixed-bed gasifiers are air-blown and produce low-energy gases (Stevens 2001).

With fixed-bed updraft gasifiers, the air or oxygen passes upward through a hot reactive zone near the bottom of the gasifier in a direction counter-current to the flow of solid material. Exothermic reactions between air/oxygen and the charcoal in the bed drive the gasification process. Heat in the raw gas is transferred to the biomass feedstock as the hot gases pass upward, and biomass descending through the gasifier sequentially undergoes drying, pyrolysis, and finally gasification. Fixed-bed updraft gasifiers can be scaled-up; however, they produce a product gas with very high tar concentrations. This tar should be removed for the major part from the gas, creating a gas-cleaning problem.

Fixed-bed downdraft gasifiers were widely used in World War II for operating vehicles and trucks. During operation, air is drawn downward through a fuel bed; the gas in this case contains relatively less tar compared with the other gasifier types. Fixed-bed downdraft gasifiers are limited in scale and require a well-defined fuel, making them not fuel-flexible.

Fluidized-bed (FB) gasifiers are a more recent development that take advantage of the excellent mixing characteristics and high reaction rates of this method of gas-solid contacting. Examples of the FB gasifier systems are the bubbling fluidized-bed (BFB) gasifiers, the entrained-bed (EB) gasifiers, and the circulating fluidized-bed (CFB) gasifiers.

The FB gasifiers are typically operated at 1050–1250 K (limited by the melting properties of the bed material) and are therefore not generally suitable for coal gasification, as due to the lower reactivity of coal compared to biomass, and higher required temperature (> 1550 K). Heat to drive the gasification reaction can be provided in a variety of ways in FB gasifiers. Direct heating occurs when air or oxygen in fluidizing gas partially oxidizes the biomass and heat is released by the exothermic reactions that occur. Indirect heating methods such as internal heat exchangers, using preheated bed material, or other means can also be used to drive the gasification reactions (Stevens 2001). The BFB gasifier tends to produce a gas with tar content between that of the updraft and downdraft gasifiers. Some pyrolysis products are swept out of the fluid bed by gasification products, but are then further converted by thermal cracking in the freeboard region (Warnecke 2000). The CFB gasifiers employ a system where the bed material circulates between the gasifier and a secondary vessel. The CFB gasifiers are suitable for fuel capacity higher than 10 MWth (Susta et al. 2003). The FB gasifier, and the CFB gasifier systems are given in Fig. 6.11.

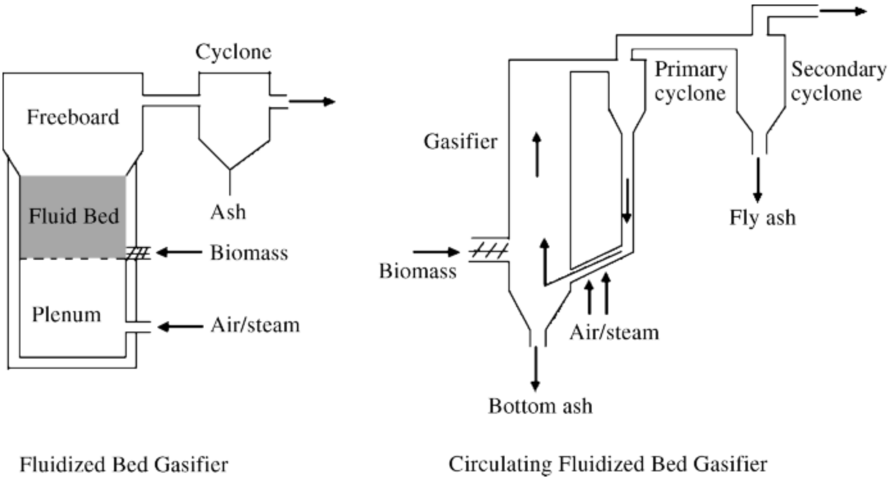


Fig. 6.20 Fluidized-bed and circulating fluidized-bed gasifier systems

6.5.2 Integrated Gasification-Fischer–Tropsch (BIG-FT) Process

The Fischer–Tropsch synthesis (FTS) was established in 1923 by German scientists Franz Fischer and Hans Tropsch. The main aim of FTS is synthesis of long-chain hydrocarbons from a CO and H_2 gas mixture. The FTS is described by (Schulz 1999):

$$nCO + (n + m/2)\,H_2 \rightarrow C_nH_m + nH_2O \qquad (6.11)$$

In the FTS one mole of CO reacts with two moles of H_2 in the presence of cobalt (Co) based catalyst to afford a hydrocarbon chain extension ($-CH_2-$). The reaction of synthesis is exothermic ($\Delta H = -165$ kJ/mol):

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \qquad \Delta H = -165\,\text{kJ/mol} \qquad (6.12)$$

The $-CH_2-$ is a building block for longer hydrocarbons. One main characteristic regarding the performance of the FTS is the liquid selectivity of the process (Stelmachowski and Nowicki 2003).

The FTS is a well-established process for the production of synfuels. The process is used commercially in South Africa by Sasol and Mossgas and in Malaysia by Shell. The FTS can be operated at low temperatures (LTFT) to produce a syncrude with a large fraction of heavy, waxy hydrocarbons or it can be operated at higher temperatures (HTFT) to produce a light syncrude and olefins. With HTFT the primary products can be refined to environmentally friendly gasoline and diesel, solvents and olefins. With LTFT, the heavy hydrocarbons can be refined to waxes or if hydrocracked and/or isomerized, to produce excellent diesel, base stock for lube oils and a naphtha that is ideal feedstock for cracking to light olefins. Biomass integrated gasification-Fischer–Tropsch (BIG-FT) process is favorable as a production route.

The FTS has been widely investigated for more than 70 years, and Fe and Co are typical catalysts. Cobalt-based catalysts are preferred because their productivity is better than Fe thanks to their high activity, selectivity for linear hydrocarbons, and low activity for the competing water–gas shift reaction. The FTS product composition is strongly influenced by catalyst composition: the product from a cobalt catalyst is higher in paraffins and the product from an iron catalyst is higher in olefins and oxygenates (Andersen 1984).

The variety of composition of FT products with hundreds of individual compounds shows a remarkable degree of order with regard to class and size of the molecules. Starting from the concept of FTS as an ideal polymerization reaction it is easily realized that the main primary products, olefins, can undergo secondary reactions and thereby modify the product distribution. This generally leads to chain length dependencies of certain olefin reaction possibilities, which are again suited to serve as a characteristic feature for the kind of olefin conversion.

While gasification processes vary considerably, typically gasifiers operate from 975 K and higher and from atmospheric pressure to 5 atm or higher. The process is generally optimized to produce fuel or feedstock gases. Gasification processes also produce a solid residue as a char, ash, or slag. The product fuel gases, includ-

Table 6.19 Typical composition of the syngas

Gaseous product	Percentage by volume
Hydrogen	29–40
Carbon monoxide	21–32
Methane	10–15
Carbon dioxide	15–20
Ethylene	0.4–1.2
Water vapor	4–8
Nitrogen	0.6–1.2

ing hydrogen, can be used in internal and external combustion engines, fuel cells, and other prime movers for heat and mechanical or electrical power. Gasification products can be used to produce methanol, FT liquids, and other fuel liquids and chemicals. The typical composition of the syngas is given in Table 6.19.

Catalytic steam reforming of hydrocarbons has been extensively studied, especially in the context of methane reforming to make syngas (H_2:CO = 2:1) for methanol and FT liquid synthesis. Methanol is produced in large quantities by the conversion of natural gas or petroleum into a synthesis gas. Biomass has also been used as a feedstock for producing synthesis gas used in production of both methanol and FT liquids.

In all types of gasification, biomass is thermochemically converted to a low or medium-energy content gas. The higher heating value of syngas produced from biomass in the gasifier is typically 10–13 MJ/Nm^3. Air-blown biomass gasification results in approximately 5 MJ/Nm^3 and oxygen-blown 15 MJ/Nm^3 of gas and is considered a low to medium energy content gas compared to natural gas (35 MJ/Nm^3).

The processing of synfuels from biomass will lower the energy cost, improve the waste management, and reduce harmful emissions. This triple assault on plant operating challenges is a proprietary technology that gasifies biomass by reacting it with steam at high temperatures to form a clean burning syngas. The molecules in the biomass (primarily carbon, hydrogen and oxygen) and the molecules in the steam (hydrogen and oxygen) reorganize to form this syngas.

Reforming the light hydrocarbons and tars formed during biomass gasification also produces hydrogen. In essence, the system embodies a fast, continuous process for pyrolizing or thermally decomposing biomass and steam reforming the resulting constituents. The entire process occurs in reducing environment biomass gasifiers. Steam reforming and so-called dry or CO_2 reforming occur according to the following reactions and are usually promoted by the use of catalysts.

$$C_nH_m + nH_2O \leftrightarrows n\,CO + (n + m/2)\,H_2 \tag{6.13}$$

$$C_nH_m + nCO_2 \leftrightarrows (2n)\,CO + (m/2)\,H_2 \tag{6.14}$$

The high-temperature FT technology applied by Sasol in the synthol process in South Africa at the Secunda petrochemical site is the largest commercial scale application of FT technology. The most recent version of this technology is the

Sasol Advanced Synthol (SAS) process. Although the FTS was initially envisioned as a means to make transportation fuels, there has been a growing realization that the profitability of commercial operations can be improved by the production of chemicals or chemical feedstock. FTS yields a complex mixture of saturated or unsaturated hydrocarbons (C_1-C_{40+}), C_1-C_{16+} oxygenates as well as water and CO_2. Laboratory studies are often carried out in differential conditions (conversions of approx. 3%) and therefore very accurate product analysis is necessary. Hydrocarbons obtained from a SAS type reactor are: for C_5-C_{10} and $C_{11}-C_{14}$ hydrocarbons, paraffins 13 and 15%, olefins 70 and 60%, aromatics 5 and 15%, and oxygenates 12 and 10%, respectively. From the component breakdown of the main liquid cuts it is clear that there is considerable scope for producing chemical products in addition to hydrocarbon fuels (Anderson 1984; Schulz 1999; Dry 2004).

The FTS in supercritical phase can be developed and its reaction behavior and mass transfer phenomenon were analyzed by both experimental and simulation methods. The same reaction apparatus and catalysts can be used for both gas phase reaction and liquid phase FT reactions to correctly compare characteristic features of diffusion dynamics and the reaction itself, in various reaction phases. Efficient transportation of reactants and products to the inside of catalysts bed and pellet, quick heat transfer, and in situ product extraction from catalysts by supercritical fluid can be accomplished.

There has been an increasing interest in the effect of water on cobalt FT catalysts in recent years. Water is produced in large amounts over cobalt catalysts since one water molecule is produced for each C-atom added to a growing hydrocarbon chain and due to the low water–gas shift activity of cobalt. The presence of water during FTS may affect the synthesis rate reversibly as reported for titania-supported catalysts, the deactivation rate as reported for alumina-supported catalysts and water also has a significant effect on the selectivity for cobalt catalysts on different supports. The effect on the rate and the deactivation appears to depend on the catalyst system studied while the main trends in the effect on selectivity appear to be more consistent for different supported cobalt systems. There are, however, also some differences in the selectivity effects observed. The present study deals mainly with the effect of water on the selectivity of alumina-supported cobalt catalysts but some data on the activity change will also be reported. The results will be compared with results for other supported cobalt systems reported in the literature (Dry 2004).

The activity and selectivity of supported Co FTS catalysts depends on both the number of Co surface atoms and on their density within support particles, as well as on transport limitations that restrict access to these sites. Catalyst preparation variables that are available to modify these properties include cobalt precursor type and loading level, support composition and structure, pretreatment procedures, and the presence of promoters or additives. Secondary reactions can strongly influence product selectivity. For example, the presence of acid sites can lead to the useful formation of branched paraffins directly during the FTS step. However, product water not only oxidizes Co sites making them inactive for additional turnovers, but it can inhibit secondary isomerization reactions on any acid sites intentionally placed in FTS reactors (Riedel et al. 1999).

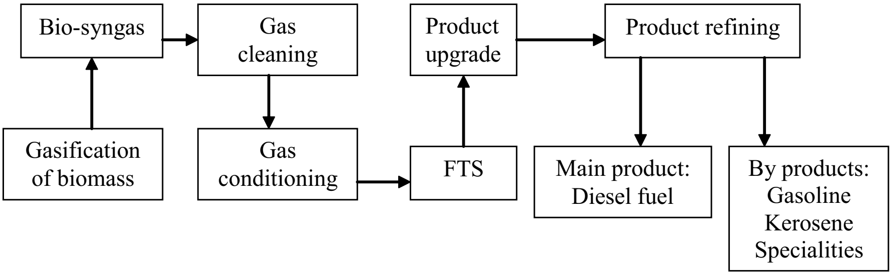


Fig. 6.21 Production of diesel fuel from biosyngas by Fischer–Tropsch synthesis (FTS)

Iron catalysts used commercially by Sasol in the Fischer–Tropsch synthesis for the past five decades (Dry 2002) have several advantages: (1) lower cost relative to cobalt and ruthenium catalysts, (2) high water–gas shift activity allowing utilization of syngas feeds of relatively low hydrogen content such as those produced by gasification of coal and biomass, (3) relatively high activity for production of liquid and waxy hydrocarbons readily refined to gasoline and diesel fuels, and (4) high selectivity for olefinic C_2–C_6 hydrocarbons used as chemical feedstocks. The typical catalyst used in fixed-bed reactors is an unsupported Fe/Cu/K catalyst prepared by precipitation (Wang et al. 2003). While having the previously mentioned advantages, this catalyst (1) deactivates irreversibly over a period of months to a few years by sintering, oxidation, formation of inactive surface carbons, and transformation of active carbide phases to inactive carbide phases, and (2) undergoes attrition at unacceptably high rates in the otherwise highly efficient, economical slurry bubble-column reactor.

It is well known that addition of alkali to iron causes an increase of both the 1-alkene selectivity and the average carbon number of produced hydrocarbons. While the promoter effects on iron has been thoroughly studied only few and on a first glance contradictive results are available for cobalt catalysts. In order to complete experimental data the carbon number distributions are analyzed for products obtained in a fixed-bed reactor under steady state condition. Precipitated iron and cobalt catalysts with and without K_2CO_3 were used (Riedel et al. 1999; Dry 2002).

Figure 6.21 shows the production of diesel fuel from biosyngas by FTS. The design of a biomass gasifier integrated with a FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid methane formation as much as possible, and convert all carbon in the biomass to mainly carbon monoxide and carbon dioxide (Prins et al. 2004).

The FTS-based gas to liquids technology (GTL) includes the three processing steps namely syngas generation, syngas conversion and hydroprocessing. In order to make the GTL technology more cost-effective, the focus must be on reducing both the capital and the operating costs of such a plant (Vosloo 2001). For some time now the price has been up to $60 per barrel. It has been estimated that the FT process should be viable at crude oil prices of about $20 per barrel (Jager 1998). The current commercial applications of the FT process are geared at the production of the valuable linear alpha olefins and of fuels such as LPG, gasoline, kerosene and diesel. Since the FT process produces predominantly linear hydrocarbons the production of high-quality diesel fuel is currently of considerable interest. The most expensive section of an FT complex is the production of purified syngas and so its composition should match the overall usage ratio of the FT reactions, which in turn depends on the product selectivity (Dry 2002).

The Al_2O_3/SiO_2 ratio has significant influences on iron-based catalyst activity and selectivity in the process of FTS. Product selectivities also change significantly with different Al_2O_3/SiO_2 ratios. The selectivity of low molecular weight hydrocarbons increases and the olefin to paraffin ratio in the products shows a monotonic decrease with increasing Al_2O_3/SiO_2 ratio. Recently, Jun et al. (2004) studied FTS over Al_2O_3 and SiO_2 supported iron-based catalysts from biomass-derived syngas. They found that Al_2O_3 as a structural promoter facilitated the better dispersion of copper and potassium and gave much higher FTS activity.

Recently, there has been some interest in the use of FTS for biomass conversion to synthetic hydrocarbons. Biomass can be converted to biosyngas by non-catalytic, catalytic and steam gasification processes. The biosyngas consists mainly of H_2, CO, CO_2 and CH_4. The FTS has been carried out using $CO/CO_2/H_2/Ar$ (11/32/52/5 vol.%) mixture as a model for biosyngas on co-precipitated Fe/Cu/K, Fe/Cu/Si/K and Fe/Cu/Al/K catalysts in a fixed-bed reactor. Some performances of the catalysts that depended on the syngas composition are also presented (Jun et al. 2004). The kinetic model predicting the product distribution is taken from Wang et al. (2003), for an industrial Fe/Cu/K catalyst.

To produce biosyngas from a biomass fuel the following procedures are necessary: (a) gasification of the fuel, (b) cleaning of the product gas, (c) usage of the synthesis gas to produce chemicals, and (d) usage of the synthesis gas as energy carrier in fuel cells. Figure 6.22 shows the green diesel and other products from biomass via Fischer–Tropsch synthesis.

6.5.3 Upgrading of Gasification Products

Main biorenewable gaseous fuels are biogas, landfill gas, gaseous fuels from pyrolysis and gasification of biomass, gaseous fuels from Fischer–Tropsch synthesis and biohydrogen (Balat 2008; Balat 2009). Figure 6.23 shows biomass upgrading by gasification and anaerobic digestion. There are a number of processes for converting of biomass into gaseous fuels such as methane or hydrogen. One pathway uses plant and animal wastes in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment. Anaerobic digestion of biowastes occurs in the absence of air, the resulting gas known as biogas is a mixture consisting mainly of methane and carbon dioxide. Biogas is a valuable fuel, which is produced in digesters filled with the feedstock like dung or sewage. The digestion is allowed to continue for a period from ten days to a few weeks. A second pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Finally, high-temperature gasification supplies a crude

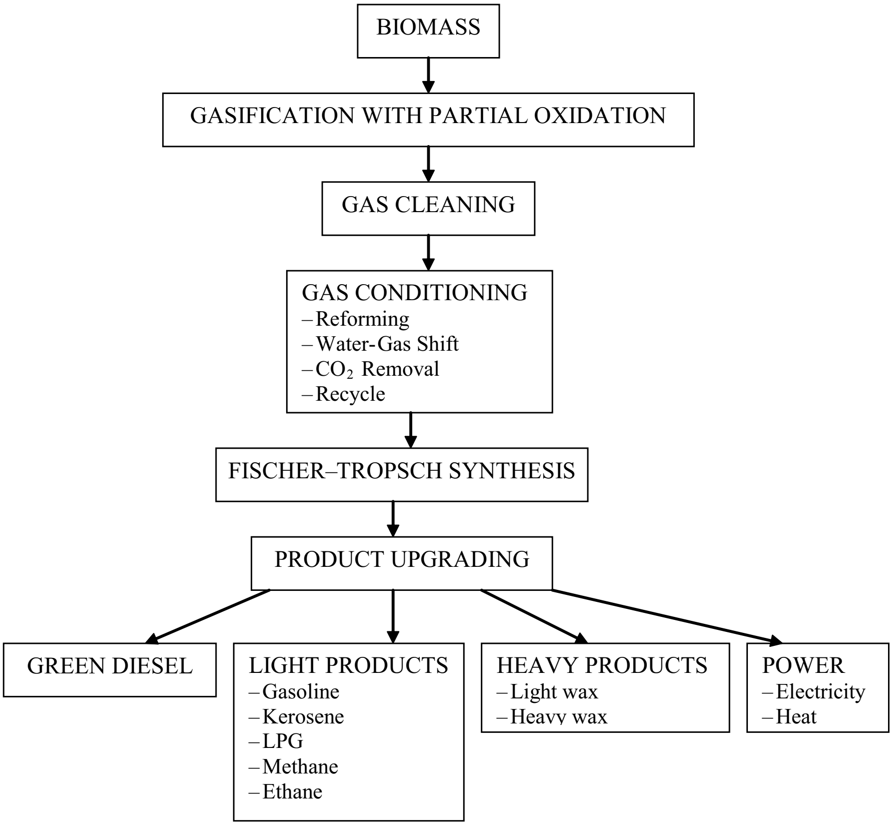


Fig. 6.22 Green diesel and other products from biomass via Fischer–Tropsch synthesis

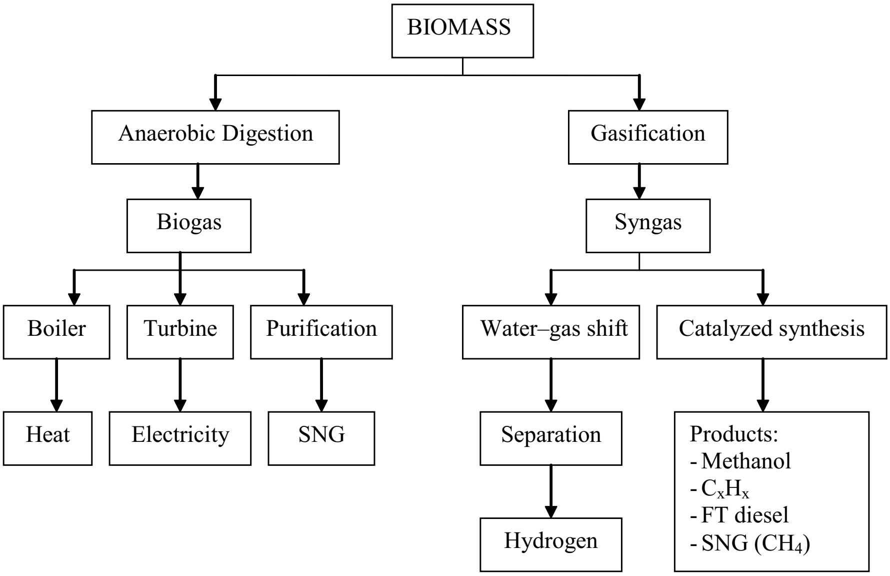


Fig. 6.23 Biomass upgrading by gasification and anaerobic digestion

gas, which may be transformed into hydrogen by a second reaction step. This pathway may offer the highest overall efficiency.

Hydrogen can be produced from biomass via two thermochemical processes: (1) gasification followed by reforming of the syngas, and (2) fast pyrolysis followed by reforming of the carbohydrate fraction of the bio-oil. In each process, a water–gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption is used to purify the product. Gasification technologies provide the opportunity to convert biorenewable feedstocks into clean fuel gases or synthesis gases. The synthesis gas includes mainly hydrogen and carbon monoxide (H_2+CO), which is also called syngas. Biosyngas is a gas rich in CO and H_2 obtained by gasification of biomass.

Hydrogen can be produced from biomass by pyrolysis, gasification, steam gasification, steam reforming of bio-oils, and enzymatic decomposition of sugars. Hydrogen is produced from pyroligneous oils produced from the pyrolysis of lignocellulosic biomass. The yield of hydrogen that can be produced from biomass is relatively low, 16–18% based on dry biomass weight (Demirbas 2001).

The strategy is based on producing hydrogen from biomass pyrolysis using a co-product strategy to reduce the cost of hydrogen and concluded that only this strategy could compete with the cost of the commercial hydrocarbon-based technologies (Wang et al. 1998). This strategy will demonstrate how hydrogen and biofuel are economically feasible and can foster the development of rural areas when practiced on a larger scale. The process of biomass to activated carbon is an alternative route to hydrogen with a valuable co-product that is practiced commercially. The yield of hydrogen that can be produced from biomass is relatively low, 12–14% based on the biomass weight (Demirbas 2005). In a proposed second process, fast pyrolysis of biomass is used to generate bio-oil and catalytic steam reforming of the bio-oil produces hydrogen and carbon dioxide.

6.5.4 Refining of Upgrading Gasification Products

Thermochemical and biochemical conversion products from biomass are upgraded before ultimate refining processes. Biorefinery includes fractionation for separation of primary refinery products. The main goals of biorefineries are to integrate production of higher value chemicals and commodities, as well as fuels and energy, and to optimize use of resources, maximize profitability, maximize benefits and minimize wastes.

The benefits of an integrated biorefinery are numerous because of the diversification in feedstocks and products. There are currently several different levels of integration in biorefineries, which adds to their sustainability, both economically and environmentally. Economic and production advantages increase with the level of integration in the biorefinery.

Biorefineries can be classified into the following categories accordingly their functions:

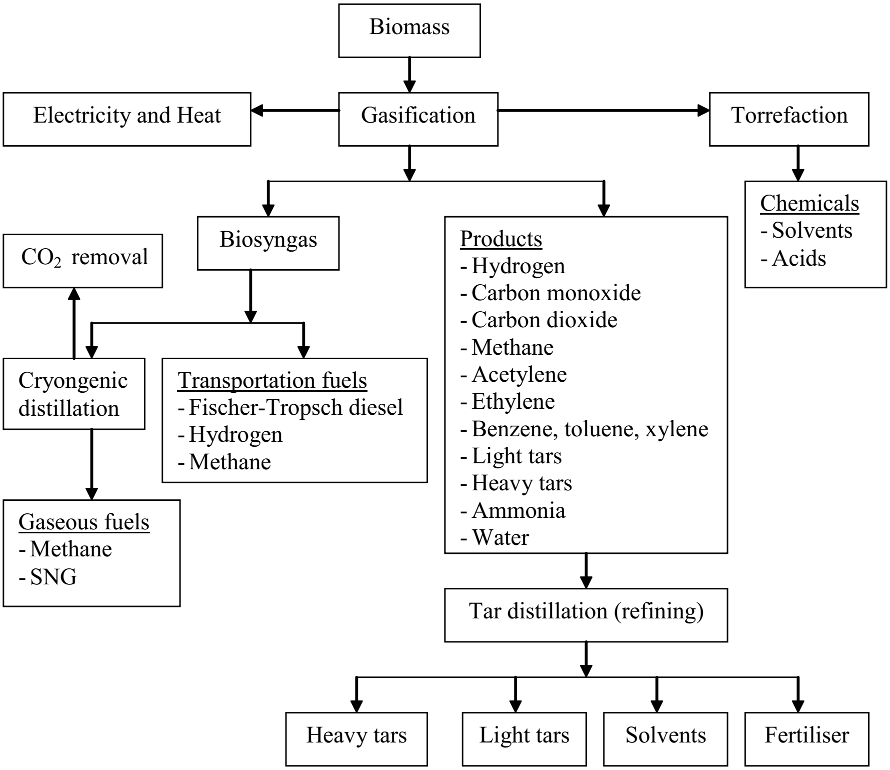


Fig. 6.24 Gasification-based thermochemical biorefinery

- Fast pyrolysis-based biorefineries
- Gasification-based biorefineries
- Sugar-based biorefineries
- Green biorefinery
- Energy crops biorefinery
- Oilseed biorefinery
- Forest-based and lignocellulosic biorefinery

Figure 6.24 shows the gasification-based thermochemical biorefinery.

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